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Science and reconstruction

The period of reconstruction now beginning must necessarily present great numbers of difficult problems. In the solution of these problems science should and will play a leading role. The obvious contributions of a material kind, such as the provision and distribution of energy, the stimulation of food production, and the exploitation of natural resources, need no expatiation here; though when information is released concerning scientific advances made during the war it will be appreciated that man's mastery of Nature has now reached a level at which the almost miraculous can be achieved. Even what has passed the censor is sufficiently arresting—coloured television, radiolocation, jet propulsion of aircraft, distant control of missiles by radio, extreme precision in the measurement of time, to name only a few items—but the whole story will seem nearly incredible.

That such command of the animate and inanimate will render the task of reconstruction immeasurably easier is patent. What is apt to be overlooked is that the application of science, on the vast scale that the situation demands, requires proportionately great numbers of scientific workers. The warring nations have maintained a varying balance between the man-power needs of the fighting services and those of supply, but it is an incontestable fact that the personnel of science is today far too meagre for the stupendous labour ahead. That is why, in any assessment of the part of science in reconstruction, the problem of recruitment and training must receive serious consideration.

As matters stand, there are three points to be noted. The first is that, owing to the war, countless young men and women who would by now have completed a course in pure or applied science, or in some technological profession, have yet to begin their training. A second point is that the distribution of young scientists among the various branches of science has for six years been rigorously 'directed' according to military requirements. In effect, this has meant that very many potential chemists and biologists have been metamorphosed into physicists, so that chemistry and biology are likely to suffer from a shortage of numbers until new students have passed through the universities and colleges. Thirdly, it is important to remember that many elderly scientists, who have patriotically postponed retirement in order to serve their country, will be lost to active science at the conclusion of hostilities.

These facts, which are true not only of Great Britain but of the Allied Nations as a whole, demand earnest attention; for reconstruction is bound to be a protracted affair, and to effect it as smoothly and swiftly as possible a long-term policy is essential.

It is clear that, in the provision of adequate numbers of scientists, one of the key factors is the supply of teachers. There are many claims for priority in demobilization, and there will be much urgent semi-military work for scientists even after the last shot has been fired; but it does not require much foresight to perceive that the early release of teachers of science from Government services, belligerent or non-belligerent, must bring results of much greater importance than the release of a similar number of most other categories. Given enough teachers, three or four years would see the beginning of that steady flow of young scientists so imperatively needed for the rebuilding of civilization, for the restoration of a worthy standard of living, and for further progress in the future.

Complementary to staff is equipment, for science cannot be divorced from the laboratory. Existing accommodation will certainly not suffice to hold the thousands of new recruits whom we

may confidently hope and expect to join the army of science as soon as conditions permit. The word 'planning' has acquired a suspiciously dictatorial ring in the ears of free men, but here is a case in which a coming need is manifest and could therefore be provided for in advance. Elaborate and permanent buildings will be unnecessary, at least for a time, and satisfactory temporary laboratory accommodation could be arranged in military huts, works, and factories no longer required for their original purposes. To see that such arrangements are put in hand is perhaps the business of the State, but governments are not in general fully conscious of the preponderating importance of science in the work that lies before us, and have been known to respond to those that make the most clamour. It therefore behoves scientists not to leave the matter to other people, but to take steps themselves to ensure that the coming influx of science students shall be given every reasonable facility for proper training.

Another case in which scientists might even already begin to exert pressure is towards securing the abolition of the 'direction' mentioned earlier. In the mortal peril of war, we readily allowed our young scientists to be set at whatever scientific or technical task the advisers of the Government thought fit. Continuance of this compulsory allocation after the war would be a disaster to science, as well as a negation of that principle of freedom for which the Allies have fought. The young scientist must be able to feel himself, like the poet, 'free as a bird to settle where I will' in the fields or groves of science; for only so will the vigour and fertility of scientific inquiry be maintained. No one can foresee how the relative importance to society of the various branches of science will change, and deliberately to starve some of them in order to fatten others is surely a grave error of judgment. The history of science shows that social needs have always evoked adequate response from scientific workers, but the absence of compulsion has left room for unfettered pursuit of knowledge—a pursuit which in the past has produced greater results than research directed to specific ends.

By removing restrictions on a scientist's choice of work, the State would not, however, absolve itself from the duty of making financial contributions for the nurture of science. It has become only too painfully clear that the very existence of a modern state depends upon science, pure and applied; and that that dependence will grow rather than diminish in the future. Whatever fraction of a tax-payer's burden is devoted to the encouragement of science, he may have the satisfaction of feeling that this part of his money is being spent for him in the way most likely to assure his well-being and safety.

Lastly, in reflecting upon some of the ways in which science is concerned in reconstruction, we are confronted once again with the recurrent problem, ever growing in urgency, of how to bring men to the proper use of the power with which science has endowed them. As has more than once been emphasized in these pages, scientists have a special responsibility in the matter, but that responsibility is still not being fully discharged. More individual and concerted propaganda is needed, of a type to familiarize the public not so much with scientific facts as with the spirit and temper of science. A good deal is being done, by the universities, the learned societies, and some industrial firms, but there is room for far greater effort. And on the other side, it must be admitted that scientists are often just as content to be left in ignorance of non-scientific developments as 'laymen' are of science. Mutual understanding is necessary. We believe that in the scientific life we have discovered a path to the removal of much evil from the world and the addition of much good. Upon whom before ourselves lies the duty of guiding the steps of others along the same path?

Contributions and correspondence should be sent to the editor: E. J. Holmyard, M.A., M.Sc., D.Litt., F.R.I.C., Imperial Chemical Industries, Nobel House, Buckingham Gate, London, S.W.1. Scientists engaged in research of an interesting or important character are invited to send short notes on work in progress and results obtained.

Surface chemistry in relation to biology

E. K. RIDEAL

The behaviour of monomolecular layers of organic substances at air-water and oil-water interfaces has attracted much attention in recent years. Professor Rideal, who has himself conducted much fundamental research on the subject, shows that surface chemistry is capable of throwing light upon many biological problems, such as the nature of cell walls, the varying toxicity of similar substances, and the fuller interpretation of vital staining.

Whilst the physiologist and biologist are agreed that the whole living unit forms a biological entity, the biochemist is more particularly interested in the specialized activities of the various cycles of chemical reactions that take place in the living cell. The fact that living matter is organized raises the important question as to how far organization can affect the equilibria or chemical kinetics which are the subject of chemical inquiry.

Living matter is characterized by the fact that the bulk of it is in the colloidal state, a large fraction both of material and of energy being present in the form of dispersions, or still more highly organized films, membranes, fibres, and capillaries. It would thus seem probable that we should take the state of matter at interfaces as representative of the conditions in which chemical equilibria and chemical kinetics are operative in biological organized systems.

This point of view arose primarily from consideration of a number of simple reactions in which the effects of a homologous series of chemical reagents on some biological process were investigated. We may take as representative of experiments of this type the effects of ketones on narcosis, and of aliphatic alcohols on stopping the respiration of cells, and the germicidal powers of certain phenols and phenyl alkyl acids.

Overton and H. Meyer in examining the anaesthetic effects of ketones on the brain of tadpoles obtained the following results:

Ketone	*Critical molecular concentration for narcosis*
Acetone	0·26
Methyl-ethyl ketone	0·09
Diethyl ketone	0·029
Methyl-propyl ketone ..	0·019
Methyl-phenyl ketone ..	0·001

Similarly, Warburg found that alcohols caused the respiration of sea-urchin eggs to cease, the inhibiting activity rising rapidly with increasing molecular weight of the homologues, as is noted in the following data:

Alcohol	*Molecular concentration for cessation of oxidation*
Methyl alcohol	5
Ethyl alcohol	1·6
Propyl alcohol	0·8
Iso-butyl alcohol	0·15
Iso-amyl alcohol	0·045
Heptyl alcohol	0·01

Overton originally advanced the view that the narcotic action of these drugs was due to their lipoid solubility, i.e. their solubility in fat-like substances; but it was shown conclusively by Warburg and his co-workers that this factor could not be generally operative, since combination could be observed even if the tissues were freed from lipoids by boiling with alcohol and ether. It was Traube who first drew attention to the fact that the narcotic activity of different alcohols varied with their power of lowering the surface tension of water, i.e. with the extent to which they were positively adsorbed at an air-water interface. This parallelism is still more marked if we consider the germicidal activity of a series of phenyl alkyl acids. In the following table I have calculated from the data of Daniels and Lyons the modified Rideal-Walker coefficient[1] of a series of these acids on *B. coli*, together with their surface tension depressant action. We note the close parallelism between surface activity and germicidal action.

[1] The Rideal-Walker test is a method by which the germicidal powers of a substance are compared, under standard conditions, with those of phenol. A Rideal-Walker coefficient of 16, for example, indicates a germicidal activity 16 times as great as that of phenol.

Acid	*Surface tension at 27° for N/500 solution: dynes/cm.*	*Depression of surface tension*	*Modified R-W phenol coefficient on B. coli*
Phenyl acetic acid ..	68	4	16
Phenyl propionic acid	66	6	17
Phenyl butyric acid	62	10	18
Phenyl valeric acid ..	56	22	21
Phenyl caproic acid	46	26	25

Matters, however, are not usually as simple as presented by the above cases. To give one instance, I may cite data presented by Albert and derived from Frobisher's investigations on the germicidal activity of certain substituted resorcinols. Whilst in the case of *Staphylococcus aureus*

Substance	*Phenol coefficient*		*Surface tension of a 0·01 per cent. solution: dynes/cm.*
	Staphylococcus aureus	*B. typhosus*	
Resorcinol	0·3	0·3	76
4–propyl resorcinol	3·7	5·0	73
4–butyl resorcinol ..	10	22	66
4–amyl resorcinol ..	30	33	60
4–hexyl resorcinol ..	98	50	54
4–heptyl resorcinol	280	30	43
4–nonyl resorcinol ..	960	0	Not recorded

the capillary activity and germicidal powers reveal the expected relationship, this is not the case for their action on the Gram-negative bacterium *B. typhosus*, where an optimum activity is noted for a chain of *ca.* six carbon atoms. A similar maximum when 4–6 carbon atoms have been added is also noted in many other cases where the varied physiological activities of substances in homologous series have been investigated. Thus the following values for the oestrogenic activity of the stilbene derivatives of Dodds and Lawson are found. A marked drop in activity is observed

Stilbene compound	*Oestrogenic activity*
4,4′–dihydroxy	1 : 150
4,4′–dihydroxy dimethyl ..	1 : 40,000
4,4′–dihydroxy ethyl methyl ..	1 : 1,000,000
4,4′–dihydroxy diethyl	1 : 3,000,000
4,4′–dihydroxy dipropyl ..	1 : 100,000

in proceeding from the diethyl to the dipropyl derivative. It is clear that the simple formulation of Traube is not sufficient to account for such observations.

A deeper insight into the mechanism of these reactions is obtained from an examination of the properties and reactions of capillarily active monolayers at air-water and oil-water interfaces. As shown originally by Sir William Hardy and Dr I. Langmuir, the molecules at such interfaces are orientated in the sense that the polar reactive groups, such as the —COOH in organic acids, are situated in the aqueous phase, and the non-polar or lipoid-soluble portions—e.g. a hydrocarbon chain or benzene ring—in the non-aqueous hydrocarbon or lipoid phase. Thus, to take an example, if a small quantity of a fatty acid, say myristic acid, be dissolved in petrol ether and a few drops of this solution be spread upon the surface of water, the petrol ether evaporates, leaving the myristic acid in the form of a film. This film is found to be in fact a monolayer or monomolecular layer in which each molecule is orientated both in respect to its neighbours and to the substrate. The polar carboxyl head groups are immersed in the water and the hydrocarbon chains or non-polar tails are in the air above the water surface. The physical properties of monolayers of a great number of organic substances have been examined during the last twenty years,

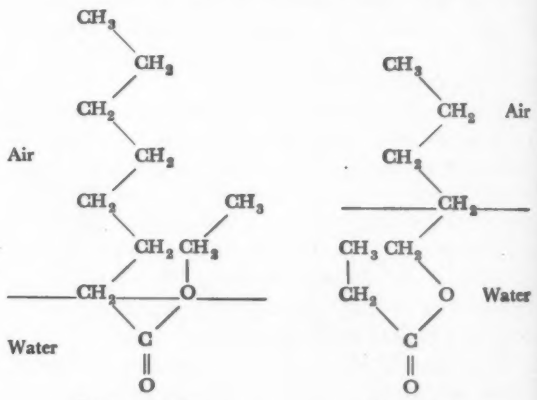

FIGURE 1 – *Orientation of molecules of ethyl caprylate and amyl propionate on water.*

and it has been shown that these can exist in the two-dimensional solid, liquid, vapour, and gaseous forms analogous to the three-dimensional systems with which we are more accustomed to deal. Critical phenomena and transitions of both the first and second order have been recorded, and latent heats of transformation evaluated. From

the biological point of view certain properties of these monolayers are of great significance. It is found that monolayers can be formed not only of a great variety of the polymeric materials which constitute the modern plastics, such as the acrylate or the vinyl resins, but also of the biologically important macromolecules, the proteins. Though some uncertainty still exists as to the exact structure of these films, it is known that the long polypeptide chains are lying horizontally at the interface in what may be called the homalic[1] state, whilst the side chains are disposed in the aqueous and lipoid phases respectively, on each side of the interface, according to their polar or non-polar characters. We obtain, in fact, a structure of three distinct layers. In the majority of cases where these protein monolayers have been examined at the air-water interface, the cohesion between the non-polar side chains and the interaction between the polypeptide backbones (probably by means of hydrogen-bonding between the —CO—NH— links) is sufficiently great to anchor at least portions of these long molecules together; we thus obtain what is in fact a two-dimensional elastic gel, the prototype of the gels met so frequently in biological systems.

The fact that the molecules at interfaces are orientated gives us an explanation of Traube's observations. It is reasonable to assume that the biological activity is a function of the amount of substance adsorbed at a lipoid-aqueous phase interface. Now there will be a close parallelism between the amounts adsorbed at such interfaces and at an air-water interface, since in the latter case the portion of the molecules exposed to the air phase are hydrocarbon in character and thus create a thin layer of lipoid-like material. In fact, the only difference to be noted between adsorption at hydrocarbon-water and air-water interfaces is that the contribution of the non-polar portion of the adsorbed molecules to their mutual cohesion or interaction is eliminated in the hydrocarbon-water interface; in consequence the film is more expanded or gaseous.

We have noted that at phase boundaries, e.g. at the surfaces of membranes, there exists an orientated monolayer of molecules with their hydrophobic portions orientated towards the lipoid and their polar heads towards the aqueous phase. It is significant to note what changes take place in the artificial monolayers if substances are introduced under the monolayer in the aqueous phase, a repetition *in vitro* of the act of adding a drug to a system of living cells. Schulman and I found that, on the addition of even extremely dilute solutions of suitable substances underneath a monolayer, a phenomenon which we have termed 'film penetration' occurred. The injected molecules entered or penetrated into the film to make a mixed or composite film which was frequently much more stable than the original. Closer investigation revealed that the composition of the mixed or complex film was equimolecular.

The conditions for this penetration to occur are found to be such that the polar head group of the film-forming material should be able to interact with the head group of the material injected. This interaction is electrical, i.e. an ion dipole or dipole-dipole interaction, but can in many cases be described chemically by assuming a hydrogen-bonding, as is exemplified in the introduction of acids under monolayers of alcohols, or of phenol under an amine. Further, whilst short-chain acids, e.g. pelargonic acid, penetrate a film of cetyl alcohol but slowly, a long-chain acid, e.g. myristic, penetrates with great rapidity. The resulting acid-alcohol complex is evidently very stable owing to two factors; the hydrogen-bonding between the polar 'head' groups and the adlineation and interaction of the hydrocarbon tails. When we compare the principles of this penetrative mechanism with the Traube concept, we see that not all capillarily active materials necessarily penetrate, but only those selected ones in which 'head' group as well as 'tail' group interaction is possible.

Other classes of substances when injected beneath a monolayer do not penetrate it but anchor themselves to the polar head groups forming the undersurface of the monolayer; thus gallic and tannic acids are adsorbed beneath monolayers of long-chain amines and of proteins, but do not penetrate them.

Further examination of the process of film penetration has shown that the ease of penetration can be controlled by adjusting the pressure of the monolayer, i.e. by alteration of the surface or interfacial tension. By suitable compression, film penetration can be stopped. Several biologically active substances exhibit remarkable powers of penetration; thus saponin and digitonin when present to the extent of only a few parts per million penetrate films of cholesterol with great rapidity, causing an immediate rise in the surface pressure of some 50 dynes per cm. The specificity is very marked, in that these substances do not penetrate cholesterol acetate or stearate, where the polar head interaction is weakened, nor do they

[1] From ὁμαλος—a flat fish.

penetrate calciferol, where the hydrophobic portion of the molecule has been altered. Digitonin is more effective in the penetration of films of various alcohols than is saponin. The acid sulphate group, e.g. in sodium cetyl sulphate, is more reactive than the polar group in saponin or even in digitonin. Three parts per million of this substance when injected under a monolayer of an alcohol will lower the surface tension of the monolayer by some 60 dynes per cm. in a few minutes.

The specificity of the polar groups for penetration into a film of cholesterol can be determined by attaching the group to a hydrocarbon chain of given length, e.g. C_{12}, and examining the pressure attained on injection of equimolecular solutions beneath a film of cholesterol held at constant area. In this way the following series is obtained:

$$-\overset{+}{N}H_3 > -SO_4' > -SO_3' >$$
$$-COO' > -\overset{+}{N}(CH_3)_3 > \text{Bile acids.}$$

As illustrating the effect of pressure on the penetration of a monolayer by a reactant in the substrate the following example may be cited. If sodium cetyl sulphate be injected beneath a monolayer of cholesterol, penetration of the latter will take place to form a mixed or complex monolayer, provided that the monolayer of cholesterol is maintained below a certain critical compression. This pressure varies with the concentration of the sodium cetyl sulphate in the following manner:

Concentration of sodium cetyl sulphate in gm./litre $\times 10^{-4}$	*Equilibrium pressure in dynes/cm. for complex formation*
1·0	17
2·0	32
3·0	38
4·0	45
5·0	47
6·0	48

These complexes are of importance in many biological reactions. Thus sodium cetyl sulphate in dilute solution haemolyses red cells with great ease, but its haemolytic activity is removed by the addition of cholesterol, although unaffected by the addition of cholesterol acetate or calciferol. With long-chain alcohols, on the other hand, the apparent haemolytic activity is increased. Thus straight-chain sulphates and alcohols haemolyse blood cells; the long-chain alcohols are *per se* too insoluble to effect haemolysis in solution, but when they are rendered soluble by complex formation with the sulphate their activity is revealed. The sulphate acts as a carrier for the alcohol.

Several significant results are obtained on the injection of certain substances beneath monolayers of a protein. We may take as examples of such substances, saponin, long-chain fatty acids, and cholesterol respectively. In the first case there is but little interaction. It might be suggested that since saponin reacts readily with monolayers of long-chain alcohols and cholesterol, but not with protein monolayers, its lytic properties are due to its interaction with the lipoid, and especially the cholesterol, portions of the cell wall. Long-chain fatty acids, in the form of soaps, on injection under a protein form a lipo-protein complex by penetration of the fatty acid ion into the protein monolayer. On addition of more of the soap (pH 7·2) the lipo-protein monolayer is displaced or 'deterged' from the surface by a fatty acid monolayer, and enters into the bulk phase as a lipo-protein complex. This effect is more marked the longer the chain of the acid. Thus a limit is set to the biological activity of a homologous series, owing to the fact that the surface film can be penetrated and dispersed from the surface, by the capillary activity of the drug forming the penetration complex, and brought into solution. This phenomenon Schulman and I found to occur in the case of the above-mentioned 4,4′-dihydroxy dipropyl stilbene compound when injected under proteins.

The spreading of a mixture of a protein and cholesterol results in the formation of a monolayer which is a lipo-protein complex. On compression of the film the cholesterol is pushed up, and the protein pushed down into the aqueous phase. At a pressure of 21 dynes per cm. the separation is completed, and this results in a radical change in the rigidity and elasticity of the film, the film changing from a thick gel to a liquid. Eventually we obtain a film of cholesterol beneath which is anchored the monolayer of protein. On releasing the pressure, the cholesterol returns into the protein monolayer to re-form the mixed film, which immediately gels again. This ejection and restoration process can be effected several times before the system breaks down. We have noted that saponin will penetrate a film of cholesterol, but not a film of a protein; and we find—as we might anticipate—that injection of saponin scarcely affects a compressed film of the cholesterol protein monolayer, as the cholesterol is protected by the underlying protein. It will,

however, react with the complex lipo-protein film at low pressure. It has been found that the greatest change in surface viscosity on compression is obtained with a 20 per cent. lipoid concentration, which is similar to the lipoid content of natural membranes.

The discovery of substances which selectively penetrate proteins and lipoid monolayers respectively permits us to draw conclusions as to the nature of the surface of many types of biological cells. Thus the cilia of *Mytilus* appear to be mainly lipoidal and those of *Paramoecium* chiefly protein, whilst haemolysis in the mammalian blood cell can be brought about by both protein and cholesterol penetrants and must in consequence have a lipo-protein surface. We can summarize the present state of our knowledge of the analogy between film reactions and biological behaviour in the following manner. Substances which are adsorbed by protein films, such as tannin, 4,4′–dihydroxy stilbene derivatives, and dibasic long-chain ionic compounds, immobilize paramoecia, do not affect rotifera, and agglutinate red blood cells. Substances which penetrate and disperse protein films, such as long-chain ionic compounds, cytolyse paramoecia, do not affect rotifera, and haemolyse red blood cells. Substances which penetrate films of cholesterol, including long-chain ionic compounds, digitonin, and saponin, cytolyse paramoecia, do not affect rotifera, and haemolyse red blood cells. It would appear that the cell wall of rotifera differs from that of paramoecia, and may consist of a chitinous envelope rather than a protein or a lipoid. Substances which penetrate films of fatty acids, such as the salts of the bile acids, have no effect on infusoria or red blood cells, but react readily with nematocyst cells.

We have referred already to the function of complexes as a 'carrier' of a potentially active material, e.g. a long-chain sulphate for long-chain alcohols. In this case both the substances act on a protein monolayer and effect dispersal. We can draw attention to many biological similarities. Thus on the addition of small quantities of long-chain soaps to phenol the germicidal activity is markedly increased, both the soaps and the phenols readily reacting with the amino groups in the protein envelope. A long-chain amine markedly increases the rate of penetration of hexylresorcinol into intestinal worms, and soaps likewise increase the toxicity of curare. On addition of excess of the penetrant carrier there is an abrupt fall in the biological activity of toxic material. This fall is associated with the beginning of aggregation or micelle formation of the carrier in the aqueous phase. Consider for example the reaction of the system soap-phenol with bacteria. On addition of small quantities of soap a soap-phenol complex is adsorbed on the envelope of the bacterium. The phenol itself subsequently penetrates, as it can anchor itself strongly to the amino groups present in the protein envelope. On the addition of more soap, aggregates of soap molecules termed 'micelles' begin to form in the aqueous phase; the phenol dissolves in the micelle and less is available for germicidal purposes.

A somewhat different aspect of this 'complex' penetration mechanism is to be found in processes of sensitization. Thus several species of bacteria can be sensitized for lysis by cholesterol-penetrants by a prior treatment with cholesterol, which is adsorbed. Another reaction of this type is described by Peters and Wakelin, who found that the complex ovoverdin, which contains both a protein and astacin, could be split by the addition of small amounts of long-chain fatty acids, to form a lipo-protein containing soap, the astacin being displaced and set free. On the addition of calcium ions, which remove the soap by the formation of the insoluble calcium salt, the process is reversed. The same workers likewise draw attention to the fact that it seems probable that the co-enzyme in an oxidase system may be separated from the enzyme by the formation of such a lipo-protein complex.

In a somewhat brief investigation of certain blood coagulants, viz. heparin and the synthetic sulphate celluloses, we found that their biological activities ran parallel to the readiness with which they penetrated films of cholesterol, suggesting that their mechanism of operation consists in forming a heparin-cholesterol complex from the cholesterol-cephalin complex present, setting the cephalin free. It may be noted in passing that the free energy change involved in forming these penetrative complexes is of the order of some 5,000 to 20,000 calories, and that both the polar and the non-polar interactions contribute sensibly to the stability of the complex, i.e. partial specificity resides in both portions of the reacting molecules.

We have already mentioned that, besides those substances which react with and penetrate monolayers, and which possess a certain specificity in these reactions due (*a*) to specific 'head' group interaction, and also (*b*) to the adlineation of the

hydrophobic portions, in which the dispersive forces or van der Waals interaction are involved, there exists a class in which only the polar head groups interact and the molecules are anchored to the base of the monolayer, but do not penetrate it. This adsorption is accompanied by a change in the phase boundary potential and in the rigidity or viscosity of the film. Examination of various films revealed interesting changes in properties when the free amino groups in protein monolayers were brought into reaction with phenolic groups by injection of various types of phenols under the monolayer. Gallic acid reacts only slowly with a protein monolayer, but tannic acid even in very dilute solutions reacts rapidly. This tanned monolayer is no longer elastic and behaves more like a pellicle or skin. Injection of protein-dispersing agents such as sodium oleate, to which we have referred above, no longer affects these skins. We must suppose that the tannic acid is attached by more than one hydroxyl group to the amino groups of the protein, and thus links the system together by multipoint contact. The 4,4′–dihydroxy stilbenes behave in a similar manner, but, with increasing length of aliphatic chain, protein dispersion can be obtained.

Substances which are adsorbed on protein monolayers in this way are found to be those which agglutinate red blood cells and likewise kill paramoecia, without cytolysis.

Certain dyes like Janus green are found to be slowly adsorbed on protein monolayers when weak concentrations are employed. On increasing the dye concentration, the surface pressure of the monolayer begins to increase, and the dye behaves like a weak penetrating agent. Here again the film behaviour is reflected in the transition from an agglutinating to a haemolysing, or at least to a sensitizing, capacity.

In examining the effect of dyes on monolayers of different types of proteins, a closer insight into the mechanism of selective staining is obtained. It is generally supposed that the dyeing of a protein such as wool consists entirely in the formation of a salt between the acid ion of the dye and a basic amino group in the wool. But the rest of the dye molecule, i.e. the hydrophobic portion, plays an important part in the adsorptive process, and it is possible by suitable adjustment of the *p*H of the medium to obtain adsorption of the negative dye ions on to proteins when these also have negative charges. Since at a given *p*H the charge on the protein albumin differs from the charges on the globulins, it is found that a great measure of selectivity in staining of the various proteins may be obtained.

We have dealt so far with the mechanism of adsorption on to monolayers and of film penetration. These factors play a part in the ingress of chemicals into cells, i.e. in the apparent permeability of cell walls. Here another important consideration must be taken into account. In order to explain the apparent permeability of various natural membranes to both lipoidal and non-lipoidal material, the so-called mosaic theory of cell wall structure has been advanced. It is postulated that there are discrete areas of lipoid and of protein material forming the surface of the wall, and that these areas are extended in depth through the membrane. We are thus provided with separate channels of ingress for the two types of penetrants. Inspection of the data on rates of permeation reveal that these are sometimes extremely high, and suggest that we cannot be dealing with a process of normal diffusion through a layer of lipoid or of protein respectively. Attention is thus focused on the boundary between the two constituents of the mosaic. If the diffusing material is soluble in one of the phases and is at the same time capillarily active, it will accumulate at the interface. In consequence the surface concentration may be quite high for relatively weak bulk solutions. Since the rate of diffusion is proportional to the concentration gradient, we might anticipate that the rate of diffusion and thus of penetration will be greatest along the interface between the two constituents of the mosaic, the diffusing molecules having their polar heads in the non-lipoidal and their hydrocarbon tails in the lipoidal portions respectively of the mosaic. The diffusing molecules must be free to move under the osmotic gradient and for this purpose it is essential that neither their polar heads nor their non-polar chains should be anchored too firmly to immobile groups in the two portions of the cell wall. It would appear that the function of the so-called 'adjuvants' is, in many cases at least, to be preferentially adsorbed on to, and thus block up, the possible retarding groups.

The fact that the molecules at an interface are orientated implies that certain peculiarities make themselves evident when we examine the processes of chemical reactions which take place between one reactant in the form of an orientated monolayer and another distributed in one of the bulk phases. The attacking molecules have to approach and react with the reactive group in the monolayer. If the orientation of this reactive group is

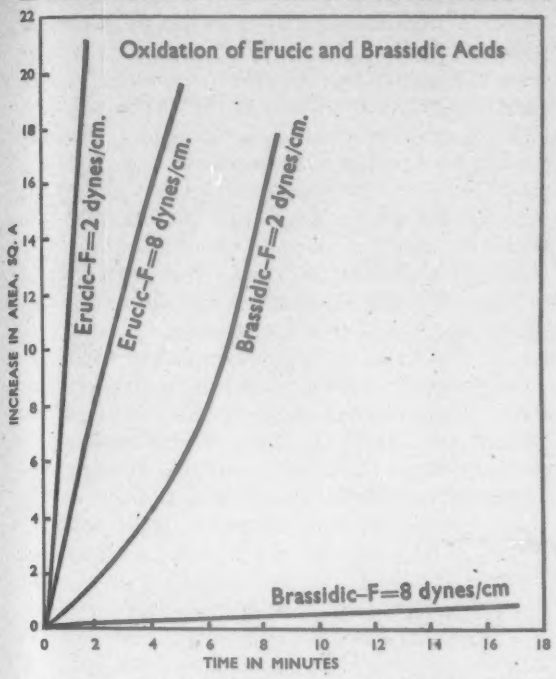

FIGURE 2 – *Oxidation of erucic and brassidic acids by* 0·005 *per cent.* $KMnO_4$ *and* N/100 H_2SO_4.

altered by tilting the molecules, i.e. by expansion or compression of the film, we might anticipate that the contours of the path of approach of the reactant would be altered. This in turn would affect the velocity of the chemical reaction.

Several examples may be given of the remarkable effects on the velocity constant of such an alteration in molecular orientation at the surface. In the graph (figure 2) is shown the effect of compression of films of the *cis* and *trans* forms of an unsaturated acid on their rate of oxidation by dilute potassium permanganate.

The difference in reactivity between the *cis* (erucic) form of the unsaturated acid, in which the long chain is bent at the double bond, and the *trans* (brassidic) form is clearly evident. It is impossible to pack the bent chains sufficiently closely together by application of pressure to prevent the access of the permanganate ion to the reactive group, but the reaction of the *trans* unsaturated acid can be almost stopped.

Another interesting reaction is to be noted in the attack of a monolayer of lecithin by the lecithinase enzyme contained in snake venom. On the injection of 0·001 per cent. black tiger snake venom beneath a film of lecithin at 20° C and *p*H 7·2 the following conversion rates of the lecithin into lysolecithin were obtained.

No. of lecithin molecules per sq. cm. $\times 10^{-14}$	*Half-life of reaction in minutes*
1·04	0·5
1·27	4
1·57	32
2·11	90

It may be noted in passing that a concentration of venom as low as $2{\cdot}5 \times 10^{-6}$ per cent. can be detected with ease by observing the effect on a monolayer of lecithin.

A simple system to which the study of phenomena occurring at interfaces can be applied is that of emulsions; it can also be appled to more specialized cases of this system, i.e. molecular aggregates and ionic micelles. If the interfacial tension be measured between oil and water in a system of the type which we have already described, where there is strong interaction or complex formation between an oil-soluble component such as cholesterol and a water-soluble component such as a long chain sodium sulphate, it is found to be so low as not to be readily measurable by normal methods (i.e. less than 0·1 dyne per cm.). If the oil-soluble component be now changed to that of a molecule which does not form a complex with the water-soluble component (or vice versa), such as cholesterol acetate in the above example, the interfacial tension is much higher. In the above case, for a saturated cholesterol acetate solution it is about 5 dynes per cm. Consequently, where there is complex formation at the oil-water interface, very little energy is required to break the interface, and where there is no complex formation the interface is reasonably stable. This means that in the former case an emulsion is formed spontaneously on shaking the oil-water system, and that the emulsion is stable, whereas in the latter system no emulsion is formed on shaking—or at the best a transient one. Thus the stability and ease of formation of oil-in-water emulsions are directly related to the degree of complex formation between the oil-soluble and water-soluble components. Furthermore, the interfacial viscosity, and the charge which is governed by the film formed by the two components, control both the overall viscosity of the emulsion and its type, viz. oil-in-water or water-in-oil. Thus where the interfacial film is rigid or highly elastic, the resultant emulsion will be a thick cream or paste,

or, if the emulsion particles are charged positively or negatively, of the oil-in-water type; but if the particles have a rigid interface and are uncharged the oil must be the continuous phase and the emulsion of the water-in-oil type.

Investigation of emulsions therefore gives us a very valuable and simple experimental tool to measure a physico-chemical analogy of the biological activity of certain chemical compounds. The chief characteristics of these compounds are that they consist of a non-polar portion, a polar group, and an ionic group, or of aggregates of these components. The mutual spacing and number of the groups control the specificity of a compound. It is very significant that proteins fall into a category fulfilling these conditions. Previous attention has been given chiefly to naturally occurring lipoids. It has been shown that analogies can be drawn between the phenomena of penetration or adsorption at oil-water interfaces by oil- or water-soluble chemical agents and the degree of their biological activity. Emulsions, since they permit of an examination of an oil-water interface in three dimensions, or bulk solution, permit us to investigate the part the electrical charge may play in surface chemical reactions and biological activity.

Thus it can be shown that globulins will adsorb on to a negatively charged emulsion preferentially to albumins, and that they adsorb in the form of a monolayer; whereas the albumins under identical conditions do not unroll at the interface but are adsorbed only in the form of a globular molecule. The salt concentration of the aqueous medium, as can be expected, plays an important role in this phenomenon. If the emulsion be positively charged it preferentially adsorbs the albumins as an adsorbed film. That with certain proteins this phenomenon is reversible can be seen from the fact that the activity of insulin and certain bacterial toxins is completely inhibited when they are adsorbed on to a negative emulsion, but returns when the emulsion is broken by means of salts or acids. Furthermore this concept is considerably extended if one replaces the emulsion by dyes, where there are many more controllable variables such as the non-polar, polar, or ionic groups in the molecule and their mutual spacing. The dye can be an aggregate of molecules where it can function as an emulsion with an interface, or a dispersed molecule or ion, where in its turn it may treat the protein molecule as the adsorbant. It is not too much to hope that by these methods we may distinguish the different proteins, nucleic acids, and lipoids in simple cells, and examine and interpret vital staining.

John Gerard—Herbalist

The influence of gardening on the development of botany as a science is well illustrated by the work of the English herbalist, John Gerard, the fourth centenary of whose birth occurs this year. Born at Nantwich, Cheshire, in 1545, he was attracted to medicine at an early age and travelled, possibly as a ship's surgeon, to Scandinavia, Russia, and perhaps the Mediterranean. By 1577, however, he had settled in London and had begun that study of plants, particularly those supposed to possess medicinal properties, which was his life's work. Besides superintending the gardens of Lord Burghley, he cultivated an extensive garden of his own at Holborn. In 1596 he published a catalogue of the plants he had grown, listing over a thousand different kinds.

The following year saw the appearance of his greatest work, the *Herball*. In this he describes 'not only the names of sundry plants but also their natures, their proportions and properties, their affects and effects, their increase and decrease, their flourishing and fading, their distinct varieties and severall qualities, as well as those which my own Countrey yieldeth as of others which I have fetched further.' The *Herball* is not an original work, being clearly based on Dodoens' *Stirpium Historiae Pemptades Sex* of 1583; but Gerard added original work of his own, as well as accounts of discoveries made by his contemporaries.

The *Herball* is a curious mixture of accurate description and contemporary folk-lore. Much of the latter, such as his circumstantial and illustrated account of a tree which produced geese as living fruit, must have strained the credulity of his readers. Despite its limitations, however, the *Herball* is valuable as a comprehensive survey of botanical knowledge and outlook at the end of the 16th century. Gerard died early in the reign of James I: the exact date is unknown.

Sir Robert John Kane

T. S. WHEELER

The son of an Irish rebel, Robert Kane became a trusted adviser of the Irish Government and received the honour of knighthood. He had achieved a European reputation in chemistry when at the age of thirty-five he attracted the attention of Sir Robert Peel, and, appointed Director of the Museum of Irish Industry and President of Queen's College, Cork, turned to education and administration. His son, Admiral Sir Henry Kane, R.N., was captain of H.M.S. *Calliope* when she made her famous escape from Samoa in 1889.

Last year Irish scientists celebrated the centenary of the publication of Sir Robert Kane's *Industrial Resources of Ireland*, a work which created a furore at the time, and was warmly praised in the British Parliament by the Prime Minister, Sir Robert Peel, and his successor, Lord John Russell. Kane himself, during his long life, gained a considerable reputation not only as an educationalist and administrator, but also as a chemist. The mineral 'Kaneite' is called after him; he anticipated Liebig in his clear recognition of the existence of the ethyl radical; he discovered the calcium chloride process for the purification of methyl alcohol; he first synthesized mesitylene from acetone; and his 'amidogene' theory of the structure of ammonia won for him a European reputation. He was the recipient of a Royal Medal, and his textbook on chemistry was in its day regarded as the best in the English language. Most of his chemical work was done before he was thirty-five years of age; Peel's recognition of his abilities then turned his steps from chemistry.

Sir Robert Kane, M.D., F.R.S., M.R.I.A.

Kane's father, John Kean (*sic*), was politically active in the 'troubles' of 1798, and had to flee to France, where he passed his exile in studying chemistry in Paris. Returning to Dublin when things had quietened, he changed his name to Kane, and set up in business as a chemical manufacturer. He prospered greatly; there is a tradition in the Irish sulphuric acid industry that 'Kane's' was the first firm in the British isles to erect and work a Gay-Lussac tower, and that they installed a number of such towers in British plants.

Robert John Kane, born in Dublin in September 1809, was John's second son. Brought up in his father's works, he naturally developed an early interest in chemistry. His first paper, polemical in nature, appeared in the *London Quarterly Journal of Science, Literature, and Art* [1] towards the end of 1828. Kane showed that the contention of a rival Dublin acid manufacturer that mineral manganese dioxide contained chlorine was incorrect; the chlorine came from hydrochloric acid which contaminated the sulphuric acid used in the experiments. The next year Kane described in the same journal [2] the natural arsenide of manganese now known as 'Kancite'; its discoverer was just twenty when he achieved immortality in this way. About this time he qualified in medicine, though he never practised.

In 1830 Kane studied pharmacy in Paris. On his return he published his first book, ***Elements of***

Practical Pharmacy. That same busy year, 1831, while still an Arts undergraduate at Trinity College, Dublin, which he had joined to improve his general education, he was appointed Professor of Chemistry in the Apothecaries' Hall, Dublin, becoming known as the 'Boy Professor.' Election to the Royal Irish Academy at the unusually early age of twenty-two followed shortly after. About this time he founded the *Dublin Journal of Medical and Chemical Science*, which still continues as a purely medical periodical under the title of the *Irish Journal of Medical Science*. For some years Kane edited the *Journal* and compiled the abstracts which were a special feature of its make-up. He also published in it a number of papers on a variety of chemical themes, and it was in the issue for 1st January, 1833 [3], that he announced his recognition of the separate existence of the ethyl radical. Liebig, developing ideas of Dumas and Berzelius, put forward the same view independently in 1834. In the subsequent dispute, Kane had no difficulty in establishing his priority. He has left it on record [4] that when his view was first put forward it was a subject for amusement and ridicule among the chemical circles in Dublin. As Professor J. R. Partington has aptly remarked, 'Their sense of humour was evidently better than their sense of judgment' [5].

In 1834 Kane was appointed Lecturer (he later received the title of Professor, which, indeed, he claimed from the beginning) on Natural Philosophy in the Royal Dublin Society; Edmund Davy, a cousin of Sir Humphry, and the discoverer of acetylene, was at this time the Society's Professor of Chemistry. Under the auspices of the Society Kane had to give courses of public lectures on various branches of physics; he also worked on the chemistry of the products obtained by the distillation of wood, and, as a result, developed his calcium chloride process for the separation of pure methyl alcohol from wood spirit. In 1837 he was able to announce to the Royal Irish Academy [6] that acetone (Kane called it 'mesitic alcohol'), which is a component of wood spirit, yielded when heated with sulphuric acid a hydrocarbon which Kane called 'mesitylene.' Although its theoretical implications were not at the time understood, this reaction of Kane's, as we now know, involved a passage from a chain to a ring compound and was fundamental in establishing the symmetry of the benzene ring. Part of this work was carried out in Liebig's laboratory at Giessen, where Kane spent the summer of 1836.

Kane also studied in detail the compounds which ammonia forms with salts of mercury, copper, and other metals. The research was everywhere hailed as important. Berzelius [7] gave it his blessing, and by 1838 Kane had established a European reputation. The theoretical basis of the investigation that ammonia is an amide of hydrogen, with one hydrogen atom differing from the other two, is no longer of interest, but the work showed much experimental skill. In 1840 Kane became editor of the *Philosophical Magazine*, and in the same year published a paper [8] on the colouring matters present in lichens which gained him a Royal Medal from the Royal Society. In 1849 he was elected to the Fellowship of the Society.

In the early 'forties, Kane issued in three parts his *Elements of Chemistry*, which, as stated on the title page, included the most recent discoveries and applications of chemical science to medicine and pharmacy and the arts. It was a great success, being a most comprehensive work extending to 1,200 pages, and written with all Kane's felicity of style. Faraday introduced it into the Army course at Woolwich, and Draper of New York University brought out in 1843 an American edition which was generally adopted in the colleges of the United States. Draper stated in his preface that the work was undoubtedly the best of its kind in English.

Busy as Kane was in these hurrying years of youthful endeavour, he very sensibly found time to get married. The future Lady Kane was Miss Katherine Baily, niece and heiress of Francis Baily, the famous English astronomer, who first described the eclipse phenomenon known as 'Baily's Beads.' Katherine Baily was brought up in Ireland, where her father held a post as a distiller. She was a botanist of merit, and at the age of twenty-two published anonymously the *Irish Flora*, a descriptive catalogue of Irish plants which was well received. One day an erring printer sent Kane a bundle of her proofs in place of his own, and, returning them in person, he met his future wife for the first time.

We come now to a turning-point in Kane's life: the publication in 1844 of his *Industrial Resources of Ireland*. The book, an expanded version of lectures delivered under the auspices of the Royal Dublin Society, was the first attempt to apply scientific methods to the evaluation and use of the industrial resources of the country. Kane dealt systematically with energy (fuel and water-power), mineral, agricultural, capital, and labour resources. The amount of detailed information he accumulated was enormous.

The book attracted the attention of Sir Robert Peel, and when, in 1845, he set up in Dublin a Museum of Economic Geology as an adjunct to the Irish Geological Survey, he made Kane Director of the Museum. Shortly afterwards he appointed Kane to the Presidency of Queen's College, Cork, one of the three constituent colleges of the Queen's University set up to provide general facilities for university education in Ireland. Kane received the honour of knighthood a few months later.

The onset of the Irish famine precluded any practical application of the scientific information on Irish industrial resources collected by Kane. He himself could devote little time to the duties of his new appointments, for the Government made extensive use of his administrative abilities in connection with the emergency measures taken to fight the famine.

When blight attacked the Irish potato crop, Peel sent over Lyon Playfair (still remembered for his statement to Queen Victoria that hydrogen and oxygen would have the honour of reacting in her royal presence) and John Lindley, Professor of Botany in University College, London, to co-operate with Kane in an inquiry into the nature of the blight and of the measures to be taken to deal with it. The problem was, of course, beyond the scientific resources of the time, and the scientists achieved nothing.

Kane was also appointed one of the eight Irish Relief Commissioners who were charged with the heavy task of supervising the general distribution of food to the starving peasantry; in addition he served on the Board of Health set up to deal with the outbreak of typhus which followed the famine.

Thus was severed Kane's direct connection with fundamental research. The remainder of his career is not without interest, in showing that the pursuit of science does not debar a man from succeeding in other fields of human activity. Until he retired in 1873, Kane devoted his energies to furthering the development of technical and university education in Ireland. When he was appointed to the Presidency of Queen's College, Cork, the Government, in view of his interest in the industrial development of the country, permitted him to retain his Directorship of the Museum of Economic Geology. Under Kane's guidance it developed into an industrial museum, its title being changed to the 'Museum of Irish Industry.' Eventually a school of applied science was attached to the institution, and in 1867 it became the Royal College of Science for Ireland. Kane thus achieved his long-cherished ambition of establishing facilities for high-grade technological instruction in Ireland. When the College was set up, the Department of Science and Art, believing, as Government departments will, that 'he who drives fat oxen need not himself be fat,' decided that 'some layman of administrative capacity, and of sufficient distinction to carry weight, but unbiased by any special scientific predilections, would. . . . be a proper head of an institution of this nature' [9], and regretted its inability to make further use of Kane's abilities. However, wiser councils prevailed, and Kane was appointed Dean of the College he had done so much to found. Simultaneously, he established and developed Queen's College (now University College), Cork.

After his retirement in 1873, Kane was appointed by the Irish Government to a number of honorary offices—Commissioner of National Education, Vice-Chancellor of Queen's University, and so on. He died in Dublin in 1890.

Few Irish chemists before or since Kane have achieved the same international reputation. In spite of his great services to the cause of education in Ireland it is, perhaps, to be regretted that he turned from chemistry at a comparatively early age.

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Teniers' alchemists

JOHN READ

It is not surprising that the romantic and mysterious atmosphere of alchemy should frequently have captured the imagination of artists. The alchemists themselves were often picturesque figures, and their laboratories seemed almost to demand interpretation on canvas. Professor Read, a leading historian of chemistry, here provides a delightful study of the alchemical paintings of David Teniers, with characteristic examples of his work.

The elder Brueghel and Stradanus were eminent harbingers of that marvellous efflorescence of Dutch and Flemish painters whose work brought so much lustre and colour and grace into the seventeenth century. Most of these artists, like their prototype, 'Farmer' Brueghel, were imbued with a deep love of the home and village life of their own peasantry. They delighted to paint genre studies of these familiar scenes, and of odd characters and quaint settings. Their keen eye for the odd and droll probably explains why so many of them turned for inspiration to that strange being, the alchemist, and his still stranger environment. Among many famous artists of this age, it is easy to single out David Teniers the younger (figure 1) as alchemy's artist *par excellence*. His lifetime covered all but the first ten and the last six years of the seventeenth century.

The Teniers family offers a remarkable example of inherited artistic ability. There were four David Teniers in direct succession, all of whom were painters; the first was born in 1582 and the fourth died in 1771, so that between them they spanned almost two centuries. The father of David Teniers the elder (b. 1582) was Julian Teniers (or Taisner), a mercer of Antwerp. His sons Julian and David both became painters, and David studied under Rubens and also at Rome. David Teniers the younger (1610–94) was born at Antwerp, and worked originally in the studio of his father, from whom he derived his inspiration and style. He may have worked in Rubens' studio also, and in 1637 he married Anna Brueghel, at that time a pupil of Rubens. A younger brother, Abraham Teniers, was also a painter of note.

David Teniers the younger painted hundreds of pictures, embracing a great variety of subjects. He is distinguished by his light and spiritual touch, the cool harmony and transparency of his colours, and his delicate rendering of the finest details. He was so versatile that 'there was no manner of painting which he could not imitate perfectly in a manner to deceive the finest connoisseurs;' but his chief interests centred in peasant life and in characters and scenes with a flavour of piquancy or drollery. He painted peasants drinking, peasants making merry, peasants at dinner, peasants playing skittles, peasants before a fire, boors regaling, peasants dancing, a peasant smoking, village fêtes and weddings, Flemish landscapes, interiors of inns, of farmhouses and kitchens, an old woman peeling a pear and another cutting tobacco, the toper, the piper, the knife-grinder, the sausage-maker, and the village doctor. The alchemist and his mysterious operations fascinated him, and he painted more than twenty pictures dealing with this inexhaustible theme.

Teniers, like so many of his contemporaries, did not lose interest in a subject when he had painted it once or twice. He had the faculty of returning time after time to the same theme, treating it from a slightly different angle each time. This feature of Teniers' work was an important factor in his prodigal creativeness. Examples of Teniers' paintings are fairly common in the large museums and galleries of art; but his alchemical paintings are known to modern chemists—if they are known at all—chiefly through reproductions in books and journals of some of the line engravings that have been made from the originals. There is a considerable variety of such alchemical engravings after Teniers and other artists, and some of them are works of great merit by talented engravers. Even the best of them, however, suffer from the unavoidable defect of giving no suggestion of the colours of the original paintings. Fortunately, a few of these paintings have been reproduced in colour by modern processes.

Another disadvantage, not always realized, is that many of the engravings are executed in

FIGURE 1 – *David Teniers*, 1610–1694. *This representation of an alchemist by Teniers is supposed to be a self-portrait.*

FIGURE 2 – *'Le Plaisir des Fous.' The 'left-handed' engraving has been reversed in the above photographic reproduction, so that the disposition agrees with that of the original painting.*
(D. Teniers Inv., F. Basan Exc.)

reverse. Some, indeed, may be seen in both right-handed and left-handed forms; incidentally, one form is sometimes scarcer and more valuable than the other! Reversed engravings may usually be identified by the recognition in them of left-handed operators. Thus, in Pierre Basan's engraving of Teniers' painting sometimes known as 'Le Grimoire d'Hypocrate' (The Black Book of Hippocrates), the central figure is stirring with the left hand and holding the Black Book in the right hand, which is clearly unnatural in a normal right-handed subject [1]. In Francesco del Pedro's later engraving of the same painting these relationships are reversed, the disposition being identical with that of the original painting, as shown in figure 3. A right-handed plate, drawn to match the original, gives a left-handed print, which is therefore easier to produce than its mirror-image. Possibly del Pedro worked from Basan's left-handed engraving, and thus reverted in his prints to the original form of the painting; alternatively, he may have cut his plate from a reflection of the original picture in a mirror.

A representative alchemical interior after Teniers is shown in figure 5, which is a reproduction of an engraving in reverse by Michon and Lorieux. This picture is markedly different from the earlier alchemical representations of Weiditz and Brueghel. The element of caricature is absent, and the central figure has a spiritual touch. The atmosphere of the laboratory is calm and orderly. The composition is brought to a focus in the alchemist. He is the central figure, illuminated by a beam of light from the open window. He is not working *en famille*: there are no distractions. The laboratory is neither a blacksmith's forge nor a converted kitchen: it is a room designed and equipped expressly for the prosecution of alchemy. There is no sign of mysticism in the form either of the apparatus of magic or of inscriptions on the walls. In brief, this picture of Teniers bears out the aphorism of Liebig: 'Alchemy was never

FIGURE 3 – *An Alchemical Interior. Sometimes known as 'Le Grimoire d'Hypocrate.'*
(From the original painting by Teniers.)

FIGURE 4 – *An Alchemist in his Laboratory.*
(From the original painting by Teniers.)

Opposite Plate – please refer to page

FIGURE 5 – *Le Chimiste.*
(Peint par David Teniers. Gravé à l'eau-forte par Michon et terminé par Lorieux.)

at any time anything different from chemistry.'

The details are rendered with the clearness and precision so characteristic of Teniers. The crucible no longer reigns supreme among the apparatus; it remains prominent, but the still is now coming into its own. Teniers' alchemists kept their apparatus, and even their books, mainly upon the floor: many pieces in glass and earthenware are so disposed in this picture. The large charcoal-bin is a characteristic feature, and so are the skull and the small painting affixed to the walls and the fish suspended from the ceiling. The suspended fish is sometimes replaced in representations of alchemical interiors by a salamander, or a crocodile; in similar pictures of doctors' consulting rooms a model of an angel is often shown in a similar position. Working after dark must have been difficult in this laboratory, as artificial light was apparently limited to two candle-power, provided by the candles fixed above and at the side of the chimney-opening.

An impression of depth is given by the figures in the background and the cat chasing a mouse in the intervening space. These are typical elements in a Teniers alchemical interior, and so is the spectator looking through the high window in the back wall.

As is usual with Teniers, the dominant colour note of the original painting lies in rich shades of brown, ranging from light browns, through red-browns, to chocolate tints. The alchemist's robe and soft hat are dark blue, trimmed at the edges with brown fur; a leather bag and a key hang from his girdle, and he wears loose slippers.

The original painting is signed by the artist and dated 1648; it measures about 21 in. by 16 in. It has had a chequered history. Before the French Revolution it was in the collection of the Duc d'Orléans, together with other paintings by Teniers. Later, it remained for many years in private ownership in England. Since 1937 it has been in the Fisher collection of alchemical and

historical pictures at Pittsburgh, Pennsylvania.

A more elaborate type of an alchemical interior by Teniers is shown in a painting in the Dresden collection (figure 4). This large laboratory has two hearths, each with a capacious chimney of masonry to carry off smoke and fumes. The hearth in the background has an open fire; this is kept alive with the help of a large pair of bellows, as in a blacksmith's forge. The smaller enclosed fires on the other hearth, in the foreground, are kept going with hand-bellows. The apparatus on this hearth is arranged in a very neat and workmanlike way; the alchemist is able to keep his crucible at the right heat and at the same time to watch a distillation from a still fitted with a two-beaked alembic.

Among the smaller accessories, the hour-glass, portable candlestick, and dried poppy heads appeal to the eye and imagination. The active cat of the smaller laboratory has been replaced by a quiescent dog, which watches the mouse with little more than formal interest. The familiar group in the background again lends an appearance of depth to the room; the central figure of this group, holding a small flask, appears to be a portrait of Teniers himself. Apart from the broken alembic lying on the floor, everything is tidily arranged; in general, the laboratory creates an impression of efficiency and purposefulness.

In this composition Teniers makes free and effective use of various shades of brown; bluish-grey tones are also prominent. The suspended fish is dull green; the glowing points of the fires, as usual, are bright red.

Some appreciation of Teniers' many variations on the alchemical theme may be gained by comparing the last-named painting (figure 4) with 'Le Grimoire d'Hypocrate' (figure 3). In the original paintings the chief figure is placed in the left foreground, facing left. There is little difference in the backgrounds of the two compositions: here, the main window, bellows, hearth, group of figures, and suspended fish are common features. In 'Le Grimoire,' the small back window with the spectator is omitted, while in the foreground the round table has been moved to the left, replacing the hearth of the other picture. Instead of the still there is a charcoal-bin, and a grindstone has been substituted for the anvil in the background.

Alchemical paintings, like others, have often been copied, sometimes with great faithfulness by pupils or admirers of the original painter[1]. Occasionally these copies are wrongly regarded as originals. In some instances the copyist has endeavoured to improve upon the original. For example, an attractive painting of 'Le Grimoire,' formerly in the collection of Sir William Pope [2], shows an extra figure of a boy standing in the empty space in the middle of the original composition (figure 3); some fresh apparatus has been put on the floor in the foreground, and a vessel and a sketch hang on the wall above the alchemist's head. This painting was attributed to 'T. Wyck,' although it is a typical Teniers composition, with none of Wyck's outstanding characteristics.

Teniers also rings the changes upon the alchemist himself. He is usually shown as an elderly and sedate man; sometimes, however, he is younger; or he may be a hunchback, or even an ape. Teniers' famous caricature (figure 2) of the lowest kind of puffer, apeing unintelligently the operations of the thinking and informed alchemist, shows an ape seated at the hearth and manipulating the bellows: it bears the satirical title, 'Le Plaisir des Fous' (The Amusement of Fools). Another composition, in complete contrast, depicts three cupids as sole tenants of the laboratory. Two of these, representing the alchemist and his famulus, are busy at the hearth, and the other is putting coins into a purse lying on the familiar round table with the ornamented tripartite foot (figures 3 and 4). A large iridescent soap-bubble hovers in the air, in the place usually occupied by the suspended fish. This charming composition is presumably based upon the *ludus puerorum* motive in alchemy, and since the purse is being filled, instead of emptied, it appears that the Great Work is indeed 'child's play' to these alchemical cupids.

[1] There is, for example, such a faithful copy in the St Andrews Collection, made by J. J. Rink in 1793, and here reproduced in colour. In 1755, the original, then 'In the Collection of Hen: Isaac Esqr.,' was engraved in reverse by T. Major, under the title of THE 'LABORATORY (i.e. The Elaboratory), and inscribed to William Pitcairn, M.D. An unreversed engraving of the same painting, by Jorma, was published in Paris, with the title 'Le Jeune Chimiste.'

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The author is indebted to Mr Chester G. Fisher, of Pittsburg, Pennsylvania, for the photograph reproduced in figure 2.

Æolian tones

E. TAYLOR JONES

The action of a steady air-current in producing vibratory movements which can give rise to musical sounds is the main topic discussed in this article. An account of the vortex theory of these movements is given, and some of its applications (including the estimation of the initial speed of a golf ball) are mentioned. A new kind of Æolian tone, different in character from those due to vortex action, is also described and explained.

The term 'Æolian Tones' was applied by the late Lord Rayleigh to sounds of definite pitch heard when the wind is blowing across a stretched string or wire, or a thin rod; or when one of these solids is moved rapidly and transversely through still air. Typical examples are the sounds of the Æolian harp, the humming of telegraph wires, and the sound of a stick or cane 'cutting the air.' Æolian tones are of no importance in music, but the theory of their mode of production has other applications and is of considerable physical interest.

When first studied by physicists these sounds were known as 'friction tones,' as they were thought to be caused by the friction of the air on the string acting as a violin bow, which sets the string into small to-and-fro movements along the hair. The vibration produced by the bow was explained by Lord Rayleigh as being due to the slight excess of limiting over sliding friction, in consequence of which the string is allowed to slip back a little when the bow begins to slide over it, and the bow does more work in the forward movement, than is done against it in the backward movement of the string, thus supplying the energy necessary for maintenance of the motion. It is not to be expected, however, that Æolian vibrations can be maintained in a similar way, since air friction increases with relative velocity of wind and wire, and greater force would be exerted by the wind in retarding the motion of the wire than in assisting it. Also it was shown experimentally by Lord Rayleigh that Æolian vibrations of a string are not parallel to the current but at right angles to it.

FIGURE 1 – *The late Lord Rayleigh.*
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The true explanation has emerged from a closer study of the steady flow of a fluid past a fixed cylinder placed in it. It is known that the fluid immediately in contact with the solid surface does not slip over it, but is at rest relatively to the solid. At a short distance from the surface, if the fluid is of small viscosity, the velocity approximates to the value in the main current, so that near the solid there is a considerable gradient of velocity transverse to the stream. In a layer having such a gradient there is a tendency to rotation, or 'vorticity,' owing to the viscous friction of the relatively moving parts of the stream, and the layer may be called a 'vortex layer.'

If the current speed is very small the retarding effect of the solid has little influence on the general nature of the flow, the fluid passing round to the back of the cylinder, and the lines of flow having nearly the same form before and

behind it. At a greater current speed, however, the fluid fails to follow the surface round to the rear, and breaks away from it at the sides, carrying the vortex layers with it, and leaving between them a region of 'dead water' sheltered by the solid from the main current. This region does not long remain quiescent, but soon becomes occupied by two vortices of opposite rotation as indicated in figure 2.

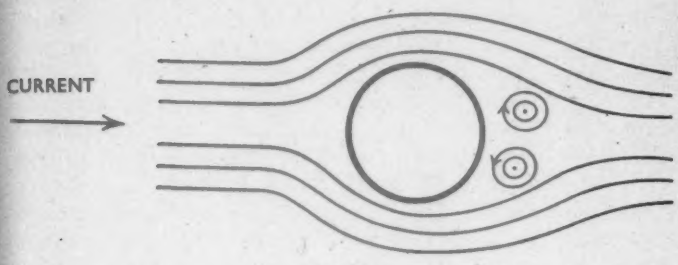


FIGURE 2

So long as the two vortices are equal in strength there is no circulation round any closed curve surrounding them and the cylinder, but if the current speed is further increased the vortices become elongated in the direction of the current, and unequal, one of them eventually breaking away from the cylinder and moving down stream as a free vortex. When this happens, circulation round the cylinder becomes established, with the result that a transverse force is caused to act upon it. A third vortex appears in place of the first, the second soon separates off to become free, and a condition is established in which the vortices are liberated alternately from the sides of the cylinder, forming two rows in the wake, not quite parallel, and not usually so regular as in the drawing of figure 3.

The velocity of the free vortices down stream is smaller than that of the main current, since each of them tends to cause the others to revolve round it, their total effect upon one of them being thus a movement against the current.

Vortex trails were described by Mallock in 1907, and by Bénard in 1908. They may be easily produced and observed by drawing a thin vertical rod horizontally through water in a basin, upon the bed of which the shadows of the surface depressions of the eddies are cast by a small source of light above the vessel. In air they may be shown by smoke figures, and in water by powder strewn over the surface: the method used by H. Rubach in photographing the wake. A stroboscopic method has been used for the study of Æolian vibrations by E. G. Richardson.

The frequency of liberation of the vortices in air depends mainly upon the current speed and the cylinder diameter, and over a wide range of values of these two quantities is approximately equal to one-fifth of their quotient. It is the periodic lateral force due to the liberation of vortices from the sides of the wire which causes it to vibrate transversely to the wind, if the frequency of the force agrees with that of one of the natural vibrations of the wire, as in the Æolian harp, or in humming telegraph wires. The strings of a violin may also be caused to sound in this way if they are slackened so as to be only just taut, and if the instrument is then held horizontally near a partly open sash window through which a rather strong wind is blowing. In these cases the tones heard are usually high overtones of the strings, the vibration of which doubtless aids the alternate separation of vortices from their two sides.

The vortex tones, however, caused by the periodic variations of pressure near the cylinder are often heard even if the cylinder does not itself take part in the vibrations, as in the 'swish' of a thin rod moved rapidly through the air. In the case of the swing of a golf club the sound heard is a mixture of tones, the highest of which is produced by the end of the shaft nearest the club head, this part being the thinnest and also moving with the greatest speed. The highest tone is easily recognizable, and its frequency is readily measured by comparison with that of a tuning fork of known frequency. An average player, for instance, may produce with a driver a tone which is a major third (ratio 5/4) above that of a 512 tuning fork, giving a frequency of 640 vibrations per second. The diameter of the shaft at its thin end being,

FIGURE 3

say, $\frac{1}{16}$ in., the velocity of this end of the shaft just before impact is found to be about 83 ft. per second. Allowance for the fact that the club head is moving rather faster than the shaft may bring the speed of the club head just before impact to about 92 ft. per second, or 63 miles an hour. A strong player can swing the club at nearly twice this speed. The velocity with which the ball is projected by the impact depends mainly upon the masses and elasticity of ball and club head, and is about 46 per cent. greater than the club head speed before impact. An average player therefore may drive the ball at 92, the strong player at about 180, miles an hour.

Professor P. G. Tait in 1896 measured the initial speed of a golf ball, driven by a good player, directly with a ballistic pendulum. The highest result found was 218 ft. per second; and this he thought, owing to the experimental conditions, was about 10 per cent. less than the player's best possible, which was therefore assumed to be 240 ft. per second, or about 164 miles an hour. But that was a gutta-percha ball. The length of 'carry' depends of course upon elevation and spin, and is much modified by air resistance.

The theory of the vortex wake has also been applied to the calculation of the resistance of a fluid to the uniform motion of a solid through it. This application was made by Kármán in 1912 for a cylinder or other elongated body moving transversely in an extended volume of fluid. The vortices being assumed to be all of the same strength, and to be arranged in two infinitely long parallel rows, with opposite rotations as in figure 3, it was shown that the configuration of such a system is stable only if the vortices of one row are opposite the mid-points between those in the other, and if the distance between the rows is a certain fraction of the spacing of the vortices in each row. This arrangement was assumed to exist in the wake at some distance from the body, the velocity of the fluid at any point in this part of the wake being calculated in terms of the main current velocity and the strength of the vortices. The latter quantity, the vortex strength, can be determined from the observed velocity of the vortices relative to the undisturbed fluid at a distance in front of the cylinder.

The eddy resistance to the motion of the body was calculated by Kármán by forming the equation expressing that the rate of increase of forward momentum in a rectangular volume enclosing the solid and some of the vortices, and moving with them, is equal to the forward force exerted by the body on the fluid *plus* the rate of flow of forward momentum through the boundary of the volume *plus* the resultant forward pressure on the boundary. The forward force of the body on the fluid is equal to the backward force of the fluid on the body, i.e. to the eddy resistance, and the other terms in the equation are all calculable from the known expressions for the fluid velocity in the wake. The formula arrived at indicates that the eddy resistance is proportional to the density of the fluid, the transverse dimension of the solid, the square of the current speed, and a numerical factor which can be determined from observations on the spacing and movement of the vortex system. Results arrived at in this way were found to agree well with certain direct measurements of the air resistance to the motion of cylinders and plates. The eddy resistance is the result of the normal pressure of the fluid upon the surface of the solid, and is quite distinct from, and usually much greater than, the so-called skin-frictional drag, which is due to tangential forces. The tendency to eddy formation, and the eddy resistance, can be much diminished by suitably tapering or stream-lining the body so as to reduce its curvature towards the rear.

The early observations on Æolian tones were made by Strouhal with an apparatus in which a wire, about half a metre long, mounted on a frame, was caused to revolve about an axis parallel to its length. A wire only some 6 in. long is, however, not very readily set vibrating in this way, but if it is replaced by a strip of thin india-rubber mounted with its plane tangential to the cylindrical surface on which it revolves, a new kind of Æolian tone is heard, louder, steadier, and better in quality than the sound of the wire. The pitch of the new tone is practically independent of the rate of revolution, and is usually that of the fundamental transverse vibration of the strip; but overtones are sometimes produced.

The new tones are not the result of vortex action, though vortices are doubtless formed at the edges of the revolving strip, and in fact at high speeds the shrill vortex tones, of pitch varying with the speed, can be heard simultaneously with the lower and steadier new tone. The vibrations giving rise to the new tones appear to be caused by the combined action of the couple and the deflecting force acting on the strip when its plane is inclined to the current of air. It was

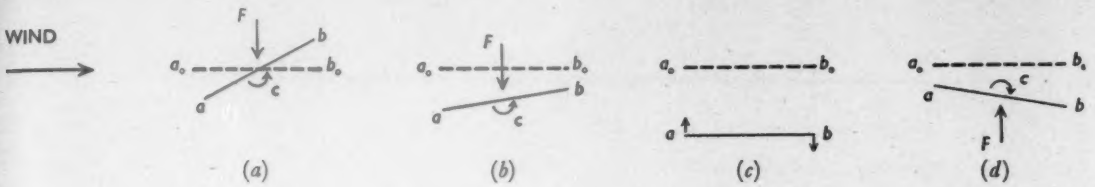


FIGURE 4

shown by Lord Rayleigh that when a disc or plate is held in this way, a couple acts upon it tending to turn it so that its plane is at right angles to the current. This well-known 'Rayleigh disc' effect may be demonstrated with a small cardboard disc mounted on a thread parallel to its plane and blown at obliquely.

The manner of the production and maintenance of the new tones is illustrated in figure 4, in which the broken line a_ob_o represents the equilibrium position of the central section of the strip. Some slight accidental rotation of the strip allows the wind, blowing from left to right, to turn it into the position ab (figure 4 (*a*)), in which the deflecting force F, i.e. the transverse component of the wind thrust, acts so as to deflect the strip to the position shown in figure 4 (*b*). The couple C and the deflecting force F both increase with the angle of rotation up to about 40°. The displacement of the strip from the equilibrium position, and therefore also the restoring force, are greater at the leading edge *a* than at *b*, so that *a* reaches its turning point before *b*. In position 4 (*c*) the strip section is again parallel to a_ob_o but the edges *a* and *b* are moving in opposite directions, and the strip is turned so that its other side is exposed to the wind, as in 4 (*d*). The deflecting force F is now reversed, and so assists the return part of the motion. It is clear that the deflecting force F is practically in phase with the transverse velocity of the strip, and is therefore able efficiently to maintain the vibratory motion. The vibration of the strip is evidently a combined flexural and torsional movement, but owing to the high tension of the strip the frequency is determined mainly by this factor and is not appreciably modified by the torsional rigidity. The rotational movement, however, plays an essential part in the maintenance of the vibration, both in giving rise to the transverse deflecting force and in causing the strip to 'tack' at the ends of the swing by turning its other side to the wind.

The new kind of Æolian tone is loudly produced when a piece of ordinary rubber band is stretched and held near the open window. With

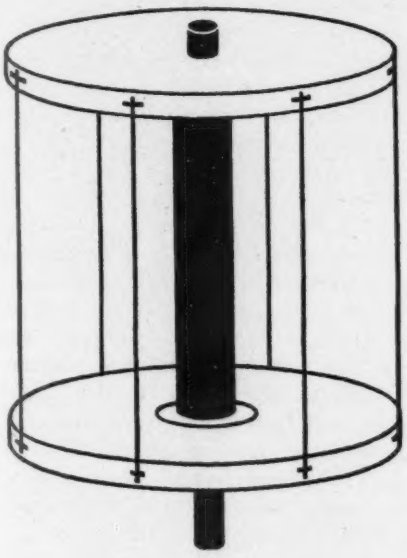


FIGURE 5

the rotating apparatus strips of thin india-rubber (the kind of which toy balloons are made), 3 or 4 cm. long and about 3 mm. wide, stretched to about six times this length, are suitable.

Figure 5 shows a six-strip rotor, the strips being attached to two coaxial wood discs about six inches apart. The strips can be easily tuned to sound any musical chord.

The root-infecting fungi

S. D. GARRETT

Fertile soil teems with living organisms, and the complexity of their interplay sets boundless problems to both scientist and cultivator. Fungi infecting the roots of plants seem on balance to be inimical to man's ends, but there is a credit side to the account. It is even possible that, when the whole story is told, judgment will be reversed.

In the microcosm of the soil, the fungi are a group of organisms second to none in numbers and importance. As saprophytes decomposing organic material on or in the soil, they break down plant remains and thus assist in transforming them into nutrients once more assimilable by green plants. As root-infecting organisms, they may sometimes be beneficial but are more frequently harmful to the growth of cultivated plants.

The evolution and ecology of the root-infecting fungi, and their relationship to the general fungus flora of the soil, can most easily be appreciated by analogy with the ecology of surface vegetation. The surface of the earth is chiefly colonized by autotrophic green plants. Except in poor habitats, unfavourable for plant growth, there is intense competition for space. Above ground, this competition for space is principally a competition for access to light; below ground, it is a competition for root-hold, water, and soil nutrients. Amongst the heterotrophic soil fungi, on the other hand, the competition is not for space, but for organic substrates. By far the greater part of the soil mass is inorganic, and thus there is great local variation in numbers of soil fungi and other micro-organisms. For instance, numbers of organisms may increase a hundredfold in the immediate vicinity of plant roots.

Organic substrates for colonization by the soil fungi and other micro-organisms are provided chiefly through the death of green plants or parts of plants. When a plant dies, its roots are quickly invaded by various soil micro-organisms, prominent amongst which are species of soil fungi. The fungi that become dominant colonists are those best fitted to decompose the particular plant tissues under the particular soil conditions obtaining. With the progress of colonization and decomposition of the substrate, the habitat is changed, so that other organisms become dominant in turn, and a succession of micro-organisms develops. As the mass of organic substrate is finite and therefore exhaustible, the end-point of the microbial succession is zero. Succession amongst soil micro-organisms developing on an organic substrate is thus somewhat different from that in surface vegetation colonizing a new habitat: the end-point of the surface succession is the climax association, or most highly developed plant community that the habitat can support.

To draw a further analogy from the ecology of surface vegetation, it will be remembered that certain open habitats, unfavourable to general plant growth, such as sand dunes, shingle banks and bare rock faces, are colonized by highly specialized plant forms. These highly specialized plants are, by virtue of their peculiar characteristics, enabled to colonize such inhospitable habitats. In this way, they have escaped from the intense competition characteristic of more favoured habitats. Amongst the soil fungi, this role of 'escapers' has been filled by the root-infecting fungi. By virtue of their special ability to open up and colonize a habitat not available to saprophytic soil fungi, i.e. the roots of living plants, they have escaped from the competition for existence as saprophytes.

Specialization has its penalties, and it is not surprising to find that the more highly specialized root-infecting fungi have little or no power of prolonged saprophytic existence in the soil. Their saprophytic existence is limited, in fact, to a somewhat precarious survival in the tissues of roots that they have invaded as parasites. This disability has been offset to some extent by the development in many root-infecting fungi of specialized survival organs, such as resting-spores and sclerotia, which serve to tide the parasite over the lean months or years. We are now beginning to understand, therefore, why specialized root-infecting fungi are not more often recorded in lists of soil fungi isolated by the agar plate method. At a disadvantage in the struggle for saprophytic existence in the soil, they are also at

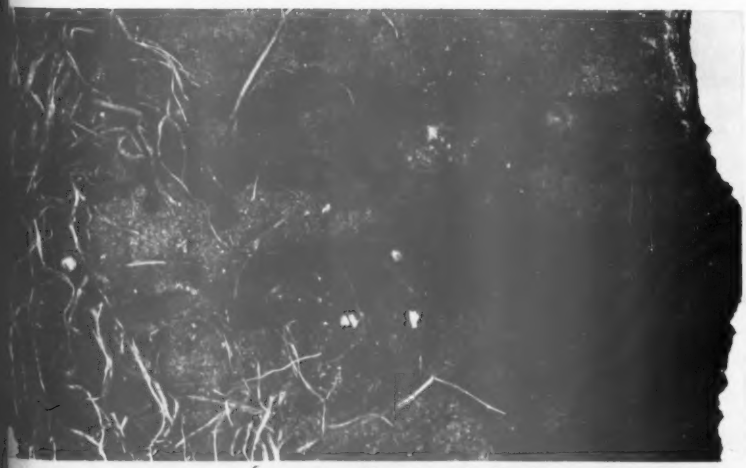
1

2

3

4

FIGURE 1 – *English barley crop affected by take-all disease.*
FIGURE 2 – *Dark-coloured threads of the take-all fungus* (Ophiobolus graminis) *growing along a wheat root.*
FIGURE 3 – *A young cabbage plant with clubroot.*
FIGURE 4 – *Dark-coloured strands of the violet root-rot fungus* (Helicobasidium purpureum) *growing over a potato tuber.*
FIGURE 5 – *Dark-coloured sclerotia of the violet root-rot fungus* (Helicobasidium purpureum) *on the surface of a sugar-beet root.*
FIGURE 6 – *Pale-coloured young strands* (*indicated by 'a'*) *of the red root disease fungus* (Poria hypolateritia), *covering the roots of a tea bush.*



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(Illustrations reproduced by permission of Rothamsted Experimental Station.)

an equal or greater disadvantage in the struggle with saprophytic fungi for development on the agar plate.

If symbiosis be the end-point of evolution in the parasitic habit, then the most highly evolved root-infecting fungi are undoubtedly the mycorrhizal fungi. In many species of green plant, infection of the roots by a mycorrhizal fungus is so normal and regular an occurrence that it has been deemed by many investigators to be obligate for the healthy growth and development of the plant. In the majority of forest trees, especially of conifers, the roots are regularly surrounded by a mantle of fungal hyphae; not only the superficial appearance but even the anatomy and internal structure of such infected roots are altered as a result of the mycorrhizal infection. Such infected roots were given the name of mycorrhiza by the first investigators of this phenomenon, in testimony to the belief that they represented a true symbiosis between fungus and root. The fungus mantle around such ectotrophic mycorrhizae replaces the root hairs as an absorbing system. In the acid humus layers of typical forest podsols, such mycorrhizae are undoubtedly more efficient than are uninfected roots, for this has been shown by experiment. Foresters, moreover, have frequently experienced great difficulty in establishing exotic coniferous trees on a new site, unless soil or humus inoculum from an old stand of the same tree, infected by a mycorrhizal fungus, has been placed in the planting holes when setting out the seedling trees.

Whereas the mycorrhizal fungus associated with roots of forest trees is mainly external, forming an ectotrophic mycorrhiza with its host plant, that associated with the roots of many species of orchids and heath plants is mainly internal, and the mycorrhiza is said to be endotrophic. Many species of orchids produce exceedingly minute seeds, and infection by the appropriate mycorrhizal fungus appears to be essential for germination and early development of the young seedling. In some saprophytic orchids, devoid of chlorophyll, this dependence upon the associated mycorrhizal fungus for nourishment drawn from the soil has been so intensified that the orchid may be considered as a parasite of the fungus!

Unfortunately for the farmer and planter, the immediate losses sometimes caused by destructive root-infecting fungi in the majority of cultivated crops far outweigh the advantages gained by the forester and orchid grower from the activities of mycorrhizal fungi. The control measures employed against these root disease fungi vary less with individual crops and fungi than with the type of cultivation, i.e. whether in field, plantation, or glasshouse. One control method alone is common to all three types of cultivation, namely the breeding and selection of varieties of crop plants resistant to disease. This method of control has been described by F. T. Brooks in a previous issue of ENDEAVOUR (1942, Vol. I, pp. 114–7), and will not be further considered here.

Basic control of root disease in annual or field crops is achieved by the practice of crop rotation, the effectiveness of which depends upon the specialization of parasitism shown by most of the root-infecting fungi. In the absence of a susceptible host crop, such fungi gradually die out from the soil, as they are unable to compete with the regular soil inhabitants for a saprophytic existence. For most effective use of crop rotation against these diseases, therefore, botanically related crops should be spaced as widely as possible in the rotation. Failure to employ an adequate rotation has been responsible in the past for such catastrophic crop losses as those from the take-all disease of wheat in Australia (*see* figures 1 and 2), and from Texas root-rot of cotton in the U.S.A. Crop rotation is least effective against those root-infecting fungi forming resting spores or sclerotia at the conclusion of their period of parasitic activity. A small percentage of such resting bodies may lie dormant in the soil for some years under non-susceptible crops, only to be awakened into activity by the roots of the first susceptible crop to be planted. Thus the single-celled resting spores of the clubroot organism (*Plasmodiophora brassicae*) may lie dormant in soil for three or four years or even longer, and then cause serious infection of a cruciferous crop (*see* figure 3). A similar function is fulfilled by the multicellular sclerotia of the fungus *Helicobasidium purpureum*, causing violet root-rot of sugar-beet and other crops (*see* figures 4 and 5). Rather long rotations are therefore required on land heavily infected by either of these parasites. Recent work has shown that the disappearance of such resting spores or sclerotia may sometimes be hastened by certain agricultural practices, such as the liberal use of green and other organic manures, the growth of certain special crops, and the use of rotary cultivators and deep-cultivating implements. By means of these and other practices (comprised under the general term of crop sanitation), whereby infected crop residues are

eliminated more quickly from the soil, the effectiveness of crop rotation can undoubtedly be much increased. Last for consideration come the palliative measures that can be applied to the growing crop, to reduce losses from those foci of infection that have escaped elimination by crop rotation and general sanitation practices. Most important of such measures is the application of artificial fertilizers; the percentage of crop yields lost through disease may often be greatly reduced by adequate nutrition of the growing crop. Another well-known palliative measure is the application of lime for control of clubroot in crucifers.

Root-infecting fungi are also of great importance in the culture of tropical plantation crops. Unfortunately for the planter, tropical plantations are usually established on the site of cleared jungle, and the root-disease fungi transfer themselves from the roots of their jungle hosts to those of the young plantation crop (*see* figure 6). A plantation may stand for many years, and no break is afforded during which the soil is free of host plant roots, as it would be under a rotation of annual field crops. Great care has therefore to be taken to eliminate infected material from the soil when clearing a site for plantation cropping.

This procedure, if carried out conscientiously, formerly entailed much expensive digging for the extraction of plant roots. Recently, however, a most original method of root disease control has been evolved by R. P. N. Napper at the Rubber Research Institute in Malaya. By Napper's method, no digging of the jungle site, and only the essential minimum of clearing, is carried out before putting in the young rubber. Subsequently, at intervals of four to six months, the young trees are inspected by a pest gang of specially trained labourers for evidence of root infection. Such inspection involves a baring of the upper tap root and laterals of every young tree. When the mycelium of a root disease fungus is discovered, it is traced to its source—a buried, infected jungle root. The infected jungle root is extracted and destroyed, but the young rubber root is usually caught at a sufficiently early stage of infection for a very simple treatment to be effective. The mycelium of the root disease fungus, which is still at this stage epiphytic or superficial, is simply pulled off, and the surface of the root is rubbed with a 2 per cent. solution of copper sulphate. The success of the method depends upon the regularity of the inspections, so that potential root infections are discovered before the fungus mycelium has actually penetrated the inner tissues of the root. In this way, the young trees are themselves employed for the discovery of dangerous sources of root disease, and much expensive digging is thereby rendered unnecessary.

A great advance in the control of root disease under tropical plantation crops may confidently be predicted from the recent discovery by R. Leach in Nyasaland that much of the root disease in young plantations arises from fungi that develop on the moribund roots of the jungle stumps *after* the jungle has been felled. After felling, as Leach has demonstrated, the roots of the stumps lose their power to resist invasion by certain parasitic fungi, which develop profusely in such roots, thence to pass to those of the young plantation crop. Leach found that if the jungle trees were killed by ring-barking, a year or so before felling, then the roots were entered not by parasites, but by harmless saprophytic fungi. From subsequent work conducted by Napper in Malaya, it seems likely that injection of the trees with certain plant poisons may be used for the same purpose.

In glasshouse cultivation, the problem of root-disease control has been met by periodical steam sterilization of the soil. The object of this soil treatment, which is more correctly described as partial sterilization, is to kill all disease-producing micro-organisms and insect pests, whilst leaving alive many of the beneficial micro-organisms. Steam treatment has the advantage over all chemical treatments so far tested that it is equally lethal to root disease fungi, to nematodes and insect pests, and to seeds of weeds. Formaldehyde, which is at present the chief competitor of steam, is ineffective against nematodes, insect pests, and most weed seeds.

Steaming also restores soil condition and fertility, and gives substantial increases in crop yield. Such increases are obtained even in soils that previously carried few injurious organisms. Partly to the activity of root-infecting fungi must be credited the adoption of soil-steaming as a routine practice by many glasshouse growers, with resulting benefit to soil condition and fertility, and therefore to crop yields. Of far greater importance, however, is the part such fungi have played in making unprofitable the monoculture of such soil-exhausting and soil-eroding crops as wheat in Australia and cotton in the U.S.A. Future agricultural historians may yet decide, therefore, that on balance the root-infecting fungi have been benefactors of mankind.

A modern interpretation of the doctrine of valency

W. G. PALMER

The classical theory of valency served chemistry well, but by rule of thumb: it was incomplete and lacked 'local detail.' Precise knowledge of atomic structure placed the problem upon an entirely new basis, and the established principles of quantum mechanics afford a means of explaining the how and the why of chemical combination. Dr Palmer makes an important contribution to our comprehension of valency in the present article.

In a recent article in ENDEAVOUR (1945, Vol. IV, p. 75) the physical principle of uncertainty has been mentioned. Scientific method, no less than a physical quantity, is subject to a similar principle, which may be expressed in the equation:

exactitude × serviceableness = a constant.

In its broad purpose of mapping the behaviour of matter, chemistry has been fortunate in the serviceableness of its cartographical principles. We may instance Avogadro's hypothesis, and the classical doctrine of valency, the former quantitatively inexact in its application to ordinary gaseous matter, and the latter an incomplete theory of chemical union. The chemical map, in fact, lacks local detail, and therefore cannot guide us with certainty in some kinds of problem increasingly experienced in modern chemistry. The purpose of this article is to show the outline of a scheme almost as simple and of as wide a scope as the old doctrine of valency, but based, as all such plans must now be, on the established principles of quantum mechanics.

The essential problem of chemistry since Dalton's time has always been to answer the questions (1) *How* do atoms combine? (2) *Why* do atoms combine? All chemical combination of atoms is attended by liberation of energy. The existence of the so-called endothermic compounds is illusory, for they are endothermic only to other more stable compounds of the same atoms. Thus ozone O_3 is more stable than the system $O + O + O$; oxygen O_2 is much more stable than the system $O + O$, but of course O_3 is endothermic to, i.e. is less stable than, O_2. Liberation of energy remains the diagnostic for chemical union, but chemistry unaided, since it cannot point to the source of the energy, cannot hope to predict in general whether given atoms will combine, and can give only a partial, empirical answer to question (2). Quantum mechanics answers this question in a more definite way, as we shall soon see, but provides to question (1) an answer which is at present unmanageable beyond the simplest molecules, at least to a chemist not already an expert in the mathematics of modern physics.

We shall first draw from quantum mechanics a picture of the actual reaction $H + H = H_2$, with questions (1) and (2) above especially in mind, and then assure ourselves from the same sources that the reactions $H_2 + H = H_3$, $He + H = HeH$, and $2He = He_2$ cannot normally take place, as they are attended by absorption

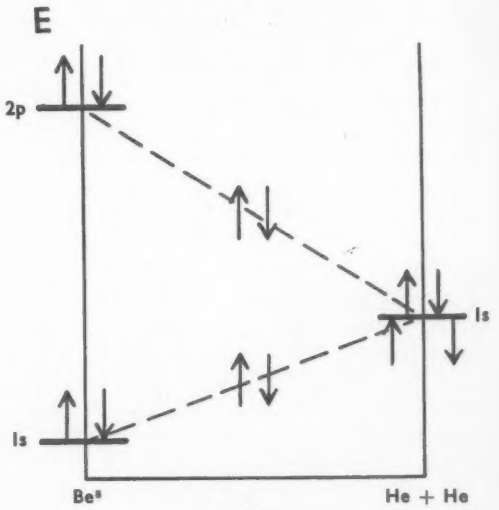


FIGURE 1

of energy. When two originally isolated atoms are brought closer together, chemical union may occur when a sufficiently small internuclear distance has been reached. Imagine the nuclei

to be forced still closer together, until they finally unite into one, the nucleus of the 'united atom.' This atom, although supposed to have been formed by an imaginary synthesis, is, like the constituent atoms, a real atom, about whose energy-levels spectroscopy provides precise information. Figure 1 indicates the original atoms as He, and the united atom as Be^4. The energy-levels associated with the orbitals of the electrons during the condensation process must be imagined to change along such lines as are shown in the figure (the lines are drawn straight only for diagrammatic simplicity), for the exclusion principle denies more than two electrons to the lowest level of any atom. The whole condensation process is obviously one of continuous energy absorption, even when the Coulombic repulsion of the nuclei is ignored. When the two original atoms are each hydrogen, the united atom will be He^2 (figure 2), but the diagram will retain the features of figure 1. If the spins of the electrons in the H atoms are in the same direction, then each must adopt a different orbital in the united atom, and again the condensation process is one of rising energy, i.e. two H atoms with 'parallel' electrons repel each other at all distances (figure 3 (*a*)). But should the spins be opposed, both electrons may and will adopt the lower *molecular* orbital of figure 2, and the condensation will occur with the liberation of energy. Remembering that the process would actually be brought to a standstill by the increasing nuclear repulsion, we see the possibility of an equilibrium inter-nuclear distance in the association of two hydrogen atoms. This is the representation of the molecule H_2 (figure 3 (*b*)). Figure 4 attempts to show the situation attending the 'condensation' of $H_2 + H$, or $He + H$. In both cases there is clearly only repulsion.

We thus derive a picture of a typical chemical bond, as found in H–H. It consists of two electrons *paired in spin* occupying one *molecular* orbital. In the system $H + H^+$, which has only one electron, this may of course enter the lower

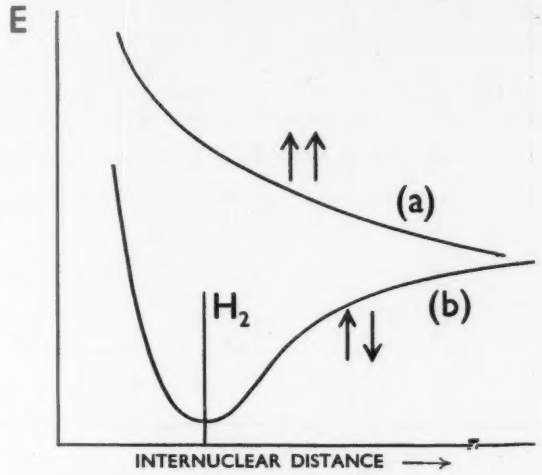


FIGURE 3

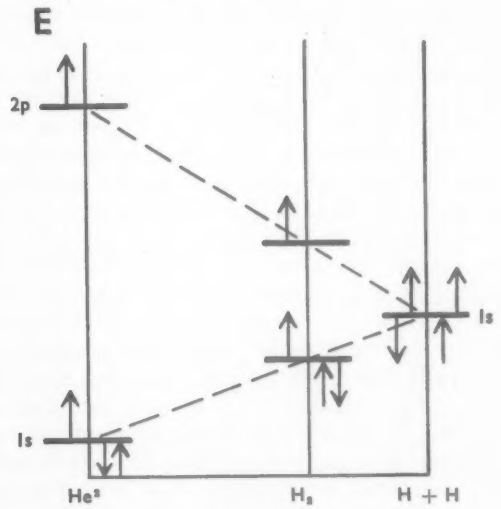


FIGURE 2

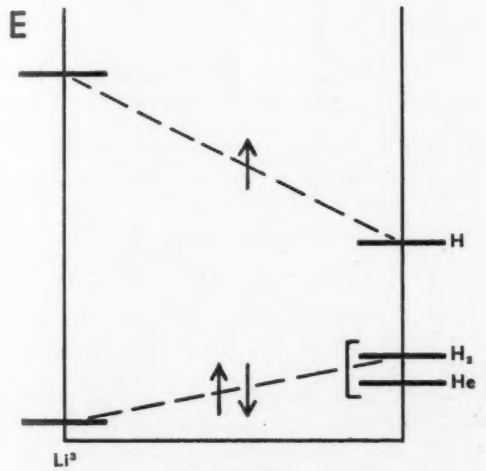


FIGURE 4

'bonding' orbital when the atom and ion approach each other. One 'lone' electron can therefore exert a bonding effect, in the molecule-ion H_2^+, but the bond will be weaker than the

TABLE I

Electron number	Normal states 1s	2s	2p$_x$	2p$_y$	2p$_z$	Excited states 1s	2s	2p$_x$	2p$_y$	2p$_z$	Atomic species
1	1										H
2	2										He, Li^+, Be^{++}, H^-
3	2	1									Li
4	2	2				2	1	1			Be
5	2	2	1			2	1	1	1		B, C^+
6	2	2	1	1		2	1	1	1	1	C, N^+, B^-
7	2	2	1	1	1	2	2	2	1		N, O^+, C^-
8	2	2	2	1	1	2	2	2	2		O, N^-
9	2	2	2	2	1						F, O^-
10	2	2	2	2	2						Ne, F^-, O^{--}

2-electron bond, as may be seen by considering the scheme

$$\begin{array}{ccccc} H & + & H & \longrightarrow & H_2 \\ \downarrow & & \downarrow & & \downarrow \\ & & I_H & & I_{H_2} \\ & & \downarrow & & \downarrow \\ H & + & H^+ & \rightarrow & H_2^+ \end{array}$$

wherein I_H and I_{H_2} stand respectively for the ionization energy of H, 13·5 electron-volts, and of H_2, 15·3 electron-volts. The difference between the energies liberated in the two reactions is clearly $I_{H_2} - I_H = 1{\cdot}8$ electron-volts. The energy of the reaction $H + H = H_2$ is well known to be 4·5 electron-volts (or 103 cal./mol.), and hence that of $H + H^+ = H_2^+$ is 2·7 electron-volts (62 cal./mol.). We conclude that the 'strength' of a one-electron bond is little more than half that of a two-electron bond. We see further that the combining power of hydrogen ceases abruptly with the formation of only one bond, as in H–H. We now propose tentatively a principle of valency. *An atom can form only as many bonds as it can provide electrons with spins not already coupled in the atom.* To apply this idea we may set out a table such as table I, in which are shown in graphic form the electronic configurations of the atoms of Series I (He and H) and Series II (Li–Ne) of the periodic system. When atoms are in process of chemical combination we are to conceive them as, so to speak, immersed in a bath of energy—the energy of formation of the compound—and part of this energy may be used to excite the atoms to higher states, if these are not too widely separated energetically from the ground, or normal, state. For this reason we show in the table not only the distribution of electrons over the available orbitals in the ground-state, but also in any excited state near the ground-state. The information on which table I is based is drawn from the detailed and exact results of atomic spectroscopy. The omission of an excited state for He does not of course mean that such states do not exist for this atom, but only that they are so very high above the ground-state that in no *chemical* action of known vigour could they be brought into play. We take the normal chemical valency therefore to correspond with the greatest number of unpaired electrons seen in either the ground or a nearby excited state. On this basis we draw up table II, showing the predicted valencies of

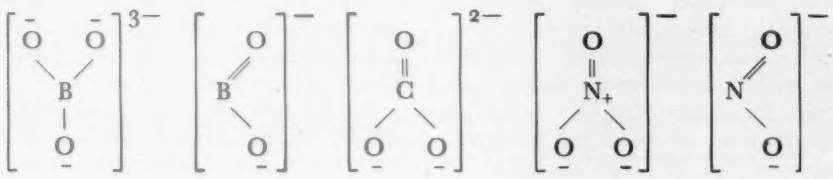
the elements in Series I and II. For H, He, Li, N, O, F and Ne the valency exerted corresponds with the ground-state; for Be, B and C the normal valencies are those of excited states. The assignment of definite valencies to ions as well as to neutral atoms will perhaps prove a novel feature to some readers, but our principle places such ions on the same footing as that of atoms. Atoms and ions of Series III (Na–Cl) are included in table II because the results of spectroscopy show that the electronic configurations of this series are similar to those of the earlier series, with change of quantum number from 2 to 3.

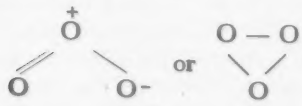
Using the principle of valency saturation long familiar to chemists, we may now construct molecules, some examples of which are shown below:

Hydrides: $(BH_4)^-$, CH_4, $(CH_3)^-$, NH_3, $(NH_4)^+$, H_2O, $(H_3O)^+$, $(OH)^-$, HF

Molecules and groups like N_2: $N \equiv N$, $\bar{C} \equiv \overset{+}{O}$, $-C \equiv N$, $-\overset{+}{N} \equiv \bar{C}$

Ions of oxyacids:



Ozone: 

Carbon dioxide: $O = C = O$, or $\overset{+}{O} \equiv C - \bar{O}$

Nitrous oxide: $N \equiv \overset{+}{N} - \bar{O}$, or $\bar{N} = \overset{+}{N} = O$

Carbon oxysulphide:

$S = C = O$, $\overset{+}{S} \equiv C - \bar{O}$, or $\bar{S} - C \equiv \overset{+}{O}$

It will be seen that our scheme of valency leads to the position that one molecular species can be assigned more than one bond-diagram, a result not new in chemistry. These alternatives are of two types: (1) as in ozone, when they have distinct shapes; (2) as in CO_2, N_2O, and COS, when they have the same (linear) form. In case (1) the correct diagram may be decided by suitable physical experiments, which show that the 'valency angle' in ozone is not 60° but nearly 120°, appropriate only to the first formula. The cases (2) are more difficult because the diagrams represent not only the same shape but practically the same energy of formation, and therefore the same stability. We must appeal again to quantum mechanics, which teaches that the total molecular electronic 'waves' of the forms will, just because they have the same energy, compound to a single wave form, and this *single* entity represents the real state of the molecule. Unfortunately we lack a convenient mode of representing pictorially such a molecular condition, and the best that can be done is to imagine all the formulae superimposed, or over-printed; but to decide the relative heaviness of the impressions we need detailed quantum mechanics. Readers of recent chemical discussions will here recognize the so-called 'resonance' or 'mesomerism.' This conclusion, that if conventional bond-diagrams are used, they are often to be considered as multiple, must be pushed further. To remain logical we must distinguish not only between O and S in COS, but between the O atoms in CO_2, $(CO_3)^=$, $(NO_3)^-$, etc. There are thus in reality groups of diagrams as shown in table IV.

When these are over-printed, each is to receive the *same* heaviness of impression, because all correspond to an identical energy of formation. In the result, CO_2 has full symmetry about a plane through the C atom, O_3 and $(NO_2)^-$ are shaped as isosceles and not scalene triangles, while $(NO_3)^-$ and $(CO_3)^=$ have full trigonal symmetry about the N or C atom. Similar reasoning leads us to give tetrahedral symmetry to XO_4 ions, such as $(SiO_4)^{4-}$, $(PO_4)^{3-}$, $(SO_4)^{2-}$, and $(ClO_4)^-$.

The scheme so far outlined sets *quadrivalency* as the maximum possible to an element. In their familiarity with very stable molecules such as

TABLE II

Valency	0	1	2	3	4
Atomic species	He, Ne	H, Li	Be, O	B, N	C
Series I *and* Series II	Li^+, Be^{++}	F	N^-	C^+, C^-	N^+
	H^-, F^-	O^-		O^+	B^-
	O^{--},				
Series III	A,	Na	Mg, S	Al, P	Si
	Na^+, Mg^{++}	Cl		S^+	P^+
		S^-			

PF_5, SF_6, P_4O_{10}, and SO_3, chemists will hesitate to accept this limitation on the combining powers of elements. Several devices have been suggested to force such molecules into the above simple scheme, such as 1-electron bonds, and ionic bonds (as in electrolytes), but they all fail in some particular. In attacking this problem we may note the valencies assigned on chemical grounds to the elements P, S, and Cl, as shown in table III.

TABLE III

Phosphorus	3 (PH_3); 5 (PF_5)
Sulphur	2 (H_2S); 4 (SO_2); 6 (SO_3,SF_6)
Chlorine	1 (HCl,Cl_2O); 3 (ClF_3); 5 (ClO_3^-); 7 (ClO_4^-).

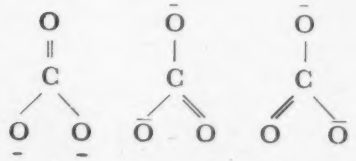
Quantum mechanics shows, and spectroscopy confirms, that for the elements Na to Cl, whose outer or 'valency' electrons lie in the 'shell' of quantum number 3, there are further available orbitals lying not too far energetically above the $3s$ and $3p$ orbitals. These are called *d* orbitals, and are five in number; when they are brought into play, table V shows that we can account neatly for all the valencies assigned above to P, S, and Cl. The empirical principle of 'odd' and 'even' valencies, long familiar to chemists, is also explained. However, the energy of 'promotion' into *d* orbitals is substantial, and hence these higher valencies are developed only when the energy of formation is large, that is, in combination with O and F. In this connection it will be recalled that sulphur forms no iodides, and that the highest bromide is S_2Br_2 (valency of S = 2).

In harmonizing the chemistry of atomic ions with that of neutral atoms we must not overlook the fact that in forming atomic ions the electrons added or removed are drawn from, or added to, other atoms or molecules. If in forming NH_4^+ from N we choose to transfer the spare electron to Cl, we have the salt NH_4Cl, and so on. We may rightly regard the ion $(SiF_6)^{--}$ as a compound of the 6-valent atom Si^{--}, which has the same electronic configuration as S.

TABLE IV

CO_2 $O = C = O$, $\bar{O} - C \equiv \overset{+}{O}$, and $\overset{+}{O} \equiv C - \bar{O}$

$(CO_3)^{--}$ and $(NO_3)^-$ ($\overset{+}{N}$ *vice* C)



O_3 and $(NO_2)^-$ ($\overset{+}{O}$ *vice* O) $O = \overset{+}{O} - \bar{O}$, and $\bar{O} - \overset{+}{O} = O$

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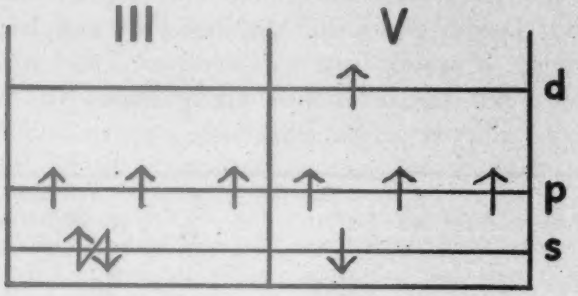
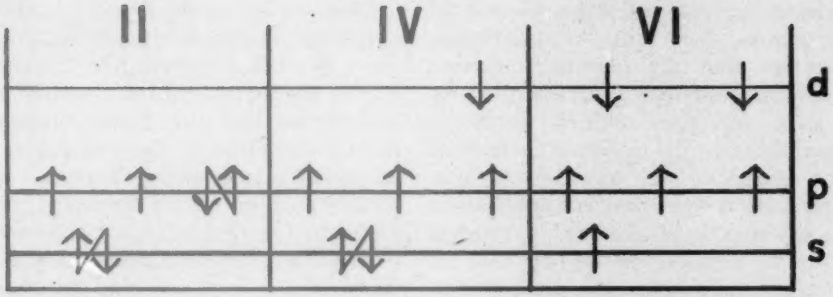
TABLE V

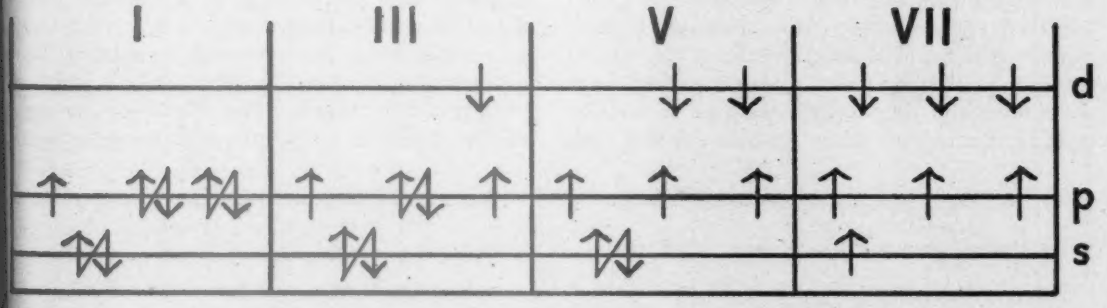
PHOSPHORUS



SULPHUR



CHLORINE



and the same available *d* orbitals, but we generally choose to draw the necessary electrons from fluorine ions, in the familiar reaction

$$SiF_4 + 2\ F^- = (SiF_6)^{--}.$$

We thus see that there is no necessity to regard the so-called 'co-ordination' compounds, of which $(SiF_6)^{--}$ is an example, as outside a simple scheme of valency.

Dissociation in salt solutions

C. W. DAVIES

The problem of the state of dissociation of salts in solution is not yet cleared up, and in this article Professor Davies shows that the theory of complete dissociation, though beguiling in its simplicity, is unsupported by the experimental facts. The nature of the undissociated part of a salt has occasioned much discussion: meanwhile dissociation constants have practical utility in several directions, some of which are here considered.

Salt solutions enter into many branches of scientific work which are far removed from pure electrochemistry. Perhaps this is why their behaviour has often been described in phrases so brief that they almost inevitably foster misconceptions. When Arrhenius' theory was generally accepted there was 'the anomaly of strong electrolytes,' which drew attention to the failure of highly dissociated substances to obey the theory, but was misleading in its implication that the treatment applied exactly to weak electrolytes. And when, about twenty-one years ago, the interionic attraction theory was established by the papers of Debye and Hückel, and Onsager, the new treatment became quickly popularized as 'the complete dissociation theory.' This title must have appreciably retarded development of the subject, for the idea that all salts in solution are completely dissociated, though unsupported by the facts, has a beguiling simplicity. Incidentally, the conception of a *completely ionized* salt probably derived more from the electronic theory of valency, and the new knowledge of crystal structure, than from any properties of solutions. The contributions of Debye and Onsager to this particular question, though very convincing and timely, were confined to demonstrating that in very dilute aqueous solution most 1–1–valent and probably some 1–2–valent salts are completely dissociated into ions.

The interionic attraction theory has been the guiding principle in much recent work on the dissociation of salt solutions, and the present article provides an opportunity for reviewing some of the facts which have accumulated.

Dissociation is most directly studied by means of conductivities. In dilute solution the conductivity of a salt is governed by the number of ions free to conduct the current and by their rate of movement. The latter factor, the mobility of the ion, itself depends on the ionic concentration, and its variation is given by Onsager's equation. As already mentioned, the decreased mobilities predicted by Onsager account for the whole conductivity change in many dilute 1–1–valent salt solutions, so that in these solutions dissociation into ions is complete. The theoretical equation is not valid, however, at concentrations much greater than one-thousandth normal, and for more concentrated solutions we must have recourse to an empirical extension of the equation, in which the square root of the concentration is replaced by a more complex function [1]. The use of this function is illustrated in table I, which shows, for the most reliable results at 25° C, the differences between

TABLE I

Concentration (g.-equiv./l.)	0·005	0·01	0·02	0·05	0·07	0·10
Lithium chloride ..	± 0·00	+ 0·03	− 0·03	+ 0·08	− 0·03	− 0·03
Sodium chloride ..	+ 0·04	+ 0·04	+ 0·03	− 0·07	—	± 0·00
Potassium chloride ..	+ 0·03	− 0·01	− 0·04	− 0·10	—	± 0·00
Hydrochloric acid ..	+ 0·01	+ 0·01	+ 0·16	+ 0·28	+ 0·06	+ 0·07
Sodium mandelate ..	± 0·00	+ 0·02	+ 0·05	+ 0·04	± 0·00	− 0·10
Potassium nitrate ..	− 0·32	− 0·63	− 1·13	− 2·34	− 3·07	− 3·79
Silver nitrate	− 0·24	− 0·45	− 0·96	− 2·38	—	− 4·13

TABLE II

MANGANESE OXALATE IN WATER AT 18° C

$m \times 10^4$	0·975	2·345	4·420	9·390	21·46	37·55
α	0·72	0·57	0·46	0·36	0·26	0·21
$K \times 10^4$	1·5	1·4	1·3	1·3	1·3	1·3

the observed conductivities and those calculated from the extended equation. The results at 18° C provide an exactly similar picture for a rather greater variety of salts.

It will be seen that even up to decinormal concentration (and probably beyond), many electrolytes (e.g. the first five of table I) obey a common equation, and this is taken as a criterion of complete dissociation; others, like the nitrates, show large deviations, the conductivity always being too low, and if we attribute the deficiency to the existence of part of the salt in a non-conducting form, it is a simple matter to calculate the fraction dissociated.

Uni-bivalent salts can be treated in the same way, except that here we have a two-stage process in which the first departures from complete dissociation can safely be ascribed to formation of the intermediate ion, $X'' + Y' = XY'$ or $X' + Y'' = XY'$.

All 2–2–valent salts appear to be incompletely dissociated even at the lowest measurable concentrations, and if Onsager's equation is accepted as a measure of the mobility changes, the fraction of salt dissociated can be easily calculated. In favourable cases the dissociation equilibrium can be studied down to quite low degrees of dissociation, as the figures for manganese oxalate show (table II). m is the concentration in g.-moles per litre, α the degree of dissociation, and K the dissociation constant.

The other main approach to the problem has been by way of electrode potentials, freezing points, and other such methods in which the equilibria studied are characterized by simple thermodynamic relationships. If a salt were completely dissociated into ions, and if the ions behaved as ideal solutes, these relationships would be exactly obeyed. Actually, of course, they are not, and the experimental results are brought into formal

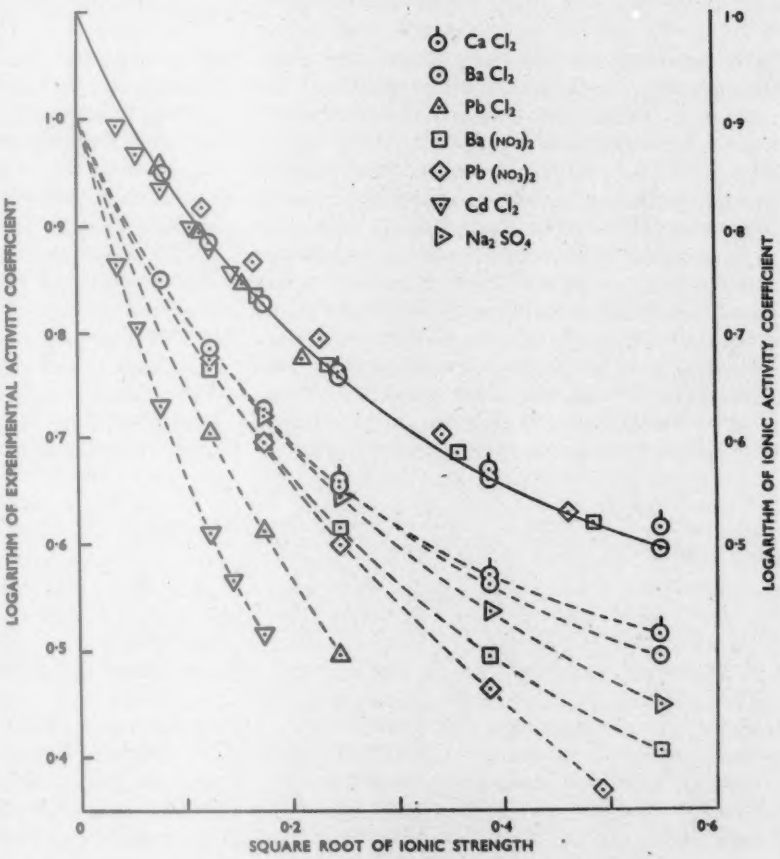


FIGURE I

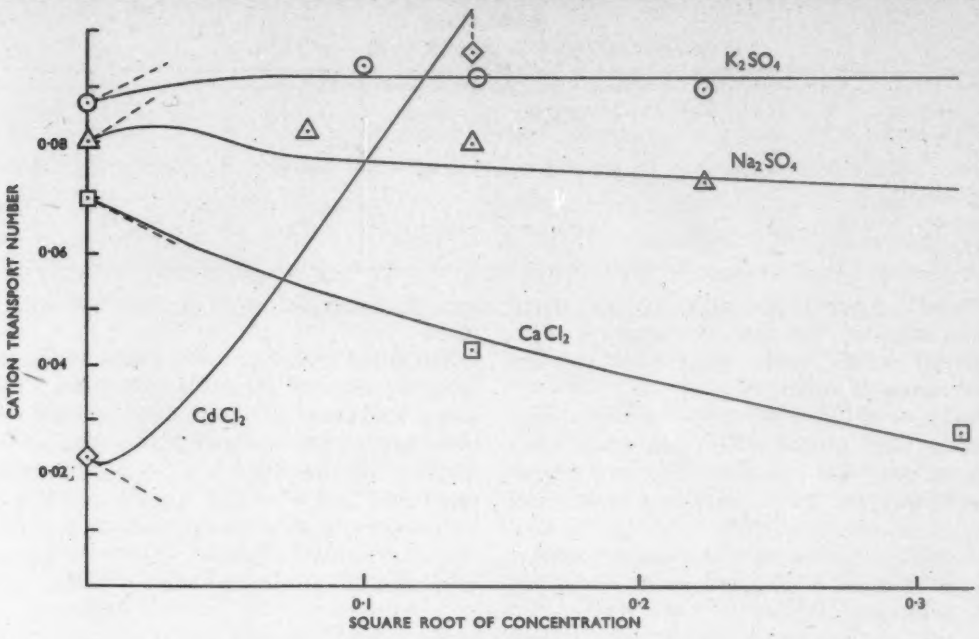


FIGURE 2

agreement with the ideal relationships by introducing activity coefficients into the equations. The activity coefficient, by which the (hypothetical) ionic concentration is multiplied, clearly has to take care of *all* causes of deviation from the ideal picture, including the effects of interionic forces, incomplete dissociation, and other departures such as even non-electrolytes show. However, there is good reason to believe that only the first two of these factors need be considered in dilute solutions, the others being comparatively unimportant at concentrations less than about decinormal. Of the two, the effect of interionic forces is given by the Debye-Hückel activity equation, with which the experimental activity coefficients should therefore agree, provided that the salt is completely dissociated. Figure 1 shows some results for ternary salts in water, the logarithm of the experimental activity coefficient being plotted (dotted lines, left-hand scale) against the square root of the ionic strength. Calcium and barium chlorides, which conductivity results show to be completely dissociated, give closely agreeing curves. The activity coefficients of the remainder are too low, but when they are corrected for incomplete dissociation by means of the conductivity data we obtain the upper series of points (right-hand scale) for the ionic activity coefficients [2]. The full curve passing through these points clearly gives us another criterion of complete dissociation extending

TABLE III

DISSOCIATION CONSTANTS OF SOME INORGANIC SALTS IN WATER

Electrolyte	*K*	*Electrolyte*	*K*	*Electrolyte*	*K*
$NaNO_2$ ..	3·8	$PbCl^+$ ..	0·030	$CaOH^+$ ..	0·031
KNO_2 ..	1·6	$PbNO_3^+$ ..	0·065	$MgSO_4$ ..	0·0070
$AgNO_2$ ..	1·5	$CdCl^+$ ..	0·010	$CaSO_4$ ..	0·0053
$KClO_2$ ..	1·4	$CdNO_3^+$ ..	0·39	$ZnSO_4$ ..	0·0047
$MgNO_2^+$ ..	*strong*	$NaSO_4^-$ ..	0·20	$KFe(CN)_6'''$ ..	0·006
$CaNO_2^+$ ..	0·52	KSO_4^- ..	0·15	$LaSO_4^+$ ..	0·00028
$BaNO_2^+$ ..	0·12	$BaOH^+$ ..	0·23	$LaFe(CN)_6$ ..	0·00018

TABLE IV

SALTS OF ORGANIC ANIONS IN WATER AT 25° C

Anion	Magnesium	Calcium	Barium	Zinc
Glycollate	0·04	0·026	0·08	0·004
Lactate	0·04	0·034	0·10	0·005
Aminoacetate	—	0·042	—	—
β-Hydroxybutyrate ..	0·09	0·15	0·14	0·03
Oxalate	0·00037	0·0010	0·0047	0·000013
Malonate	0·0016	0·005	0·007	0·00021
Succinate	0·007	0·010	0·02	0·002
Fumarate	—	0·010	0·026	—
Maleate	—	0·0037	0·0055	—
Malate	0·003	0·0022	0·0064	0·0002
Tartrate	0·005	0·0016	0·0029	0·0003

to higher concentrations than the limiting equation of Debye and Hückel, and a comparison of the activity data of other salts with this standard gives a second general method of computing degrees of dissociation.

Wherever both conductivity and activity data have been available for the same salt these two methods have shown good agreement, and the dissociation constants of a great many salts have now been determined in one or both of these ways. Other methods of more limited application are available. Thus several dissociation constants have been checked by measuring the *p*H values of suitable mixtures; and the value found for lead chloride has been confirmed by observations of the ultraviolet absorption spectra of its solutions [3].

One other type of measurement deserves mention, not because it is well adapted to the determination of dissociation constants, but because it offers perhaps the most direct test of the correctness of our assumptions. The points plotted in figure 2 show the cation transport numbers of some ternary salts in water (on an arbitrary scale), and the dotted lines indicate the changes with concentration predicted by Onsager's equation. Calcium chloride, which is completely dissociated, gives results of normal type. The data for sodium and potassium sulphates show that the increase predicted by Onsager's equation must occur at very low concentrations, where dissociation is almost complete; but that it is soon counterbalanced by a new effect, the movement of potassium or sodium away from the cathode as part of the intermediate ion. With the weaker cadmium chloride this reversal is still more pronounced, providing very definite evidence of the appearance of a new ionic species ($CdCl^+$) in the solution. The curves shown in the figure give the values calculated from the extended conductivity equation mentioned earlier, and the dissociation constants derived from it. In every case the agreement with the experimental points is good.

Table III gives dissociation constants for some of the commoner inorganic salts [1] [2] [4]. The halides of the alkali and alkaline earth metals are completely dissociated up to at least one-tenth normal concentration, but the nitrates and the sulphates are appreciably weaker. The average figure $K = 0{\cdot}005$ for the sulphates of the bivalent metals implies a degree of dissociation of not much more than 50 per cent. in a decinormal solution—though it would be wrong to assume still lower values in more concentrated solutions, since the high interionic forces in these may result in the dissociation increasing once more.

Turning to salts of organic acids, the sodium salts so far studied are completely, or almost completely, dissociated, but those of bivalent metals show wide variations, some of them being very weak electrolytes. Some typical dissociation constants are given in table IV [5], the figures in the first four rows being the dissociation constants of the intermediate ions, e.g. $(CH_2(OH).COOMg)^+$. A noteworthy effect is the weakness of the calcium salts of α-hydroxy- and α-amino-acids; in a 0·02 M-solution of calcium lactate about one-half of the acid radicle is associated with calcium in the univalent cation $Ca(Lac.)^+$. This may be of physiological significance, for the adsorption,

behaviour towards enzymes, and the Donnan equilibrium distribution of the constituents will all be greatly modified.

On the theoretical side, the nature of the undissociated part of a salt has been the subject of a good deal of discussion. If the opposite charges on cation and anion can approach one another sufficiently closely, the energy required to separate them again may be much greater than the average kinetic energy possessed by the ions, and the solution will then contain a certain proportion of non-conducting ion-pairs. It has been shown that some of the figures reported can be explained in this way without assigning unreasonable values to the effective ionic radii. For salts like magnesium sulphate or lanthanum ferricyanide this explanation seems to be the only one in keeping with the stable electronic structures of the ions, and it is supported by the general tendency of the dissociation constants to fall into groups according to the valency types of the salts considered, and to decrease with increasing valency of the constituent ions. Cutting across this, however, are other effects: the weakness of the chlorides of mercury, cadmium, and lead, for instance, cannot be explained in terms of ionic radii, and the changes in the absorption spectra of lead chloride solutions also argue that the interaction between the ions goes further than can be explained by Coulomb's law. Calcium mandelate is a similar case, where the optical rotation of the intermediate ion is found to be entirely different from that of the mandelate ion. This whole question, however, leaves the practical utility of dissociation constants unaffected, and we may now consider some of the directions in which they can be of value.

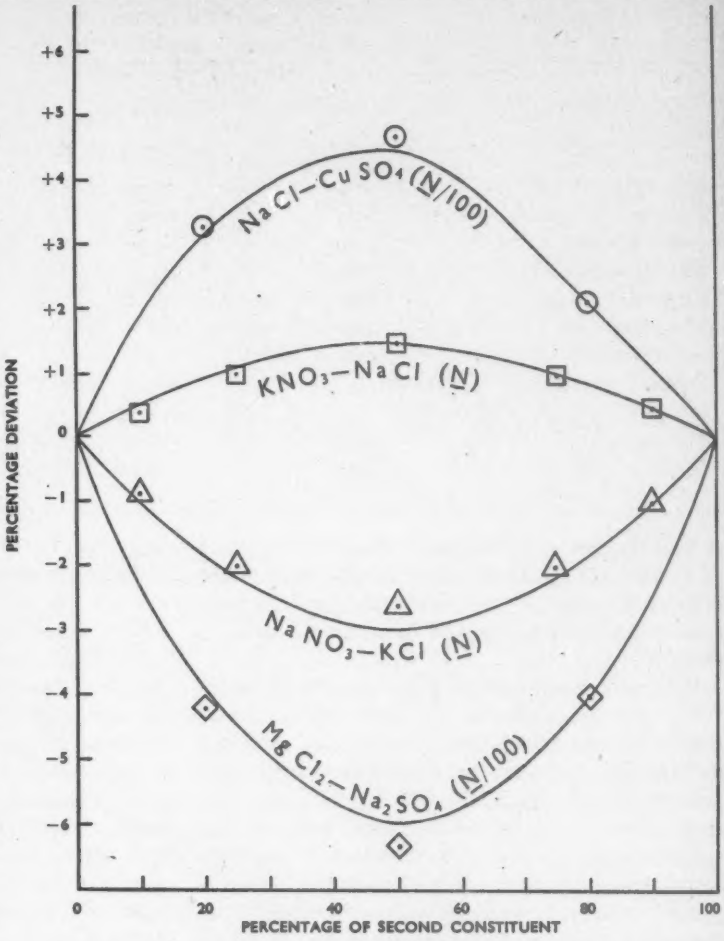


FIGURE 3

When one salt solution is added to another, the mixture will generally differ from its constituents in ionic strength, and the thermodynamic behaviour of the salts will be affected to some extent. The mobilities of the ions will also change, since they depend upon the mobilities of all the ions present. In the absence of ionic association these effects will usually be small; they can be made negligibly small by a correct choice of conditions, or can be calculated with reasonable accuracy. If, on the other hand, any pair of ions in the mixture gives rise to association products, the properties of the mixture may be greatly modified, and the additive rules so often used will lead to gross errors.

The conductivity of mixtures illustrates this well [6]. In many of the mixtures studied (at constant total concentration) the departures from additivity are small, and can be accounted for by mobility changes. But in others, some of which are illustrated in figure 3, the deviations from the ordinary mixture rule are very large, sometimes as great as 10 per cent., and on the complete dissociation theory they seem quite erratic and

unpredictable. Results like these offer no difficulty when allowance is made for incomplete dissociation: in fact, the curves in the figure show the deviations predicted by the dissociation constants in table III. The low values for the magnesium chloride-sodium sulphate mixtures are due to extensive association between magnesium and sulphate ions, whereas the chief effect on mixing sodium chloride and copper sulphate is the increasing dissociation of the latter. The other two curves are explained by the fact that potassium nitrate has a lower dissociation constant than sodium nitrate.

All the physical properties of salt mixtures are subject to similar considerations. The relative importance of the corrections for ion association vary, of course, but the additive mixture rule should be regarded with much caution, especially where multivalent ions are involved.

In the field of reaction kinetics, Cobb and Anderson [7] have reported one case where the discrepancies in the rate of a reaction in solution are attributable to ion association, and there is little doubt that many of the anomalies to be found in the literature could be explained in the same way. Particularly large changes in reaction rates may be expected where one of the reacting species undergoes ion association with a consequent change in its electrical charge.

It is probably in the use of buffer solutions that the effects of association between ions are most commonly encountered. The usual buffers are partly neutralized solutions of weak acids, and in employing them as media of constant *p*H it is assumed—on the basis of the complete dissociation theory—that the equilibria set up in them are not appreciably disturbed by small additions of other salts. How erroneous this assumption may be can be strikingly illustrated with a dilute, half-neutralized malonic acid solution, coloured with bromophenol blue. If a zinc salt solution is added to this, the colour changes rapidly—even more rapidly than would result from an equimolecular addition of hydrochloric acid—and a *p*H change of more than one unit may be produced. The reason is the extensive formation of undissociated zinc malonate, which proceeds mainly by the equation: $Zn^{\cdot\cdot} + HMal' = ZnMal + H^{\cdot}$. This is rather an extreme case, as zinc malonate is a weak electrolyte; but effects of a similar kind are to be expected whenever a salt solution is added to a buffer, at any rate when multivalent ions are present. The common phthalate, phosphate, and citrate buffers have a restricted usefulness for this reason.

In conclusion, the colorimetric determination of *p*H values may be cited as a field of work in which a closer study of the 'salt effects' would be profitable. At present *p*H values determined with indicators are regarded with some suspicion, mainly because large, and at first sight rather capricious, 'salt errors' seriously limit the accuracy of the measurement. There are four ways in which the addition of a salt can alter the reading. The first is through altering the ionic strength, and hence the activity of the hydrogen ion; the second is an effect of the type just described for zinc malonate. Both of these alter the *p*H of the solution, and are not properly 'salt errors' at all. A third is the shift in the indicator equilibrium resulting from the change in ionic strength, an effect that can be calculated; and a fourth is a change in the colour of the indicator resulting from its association with one of the added ions. There is little doubt that if these factors were given proper consideration, the indicator method would offer, at any rate in favourable cases, a simpler and more precise method of *p*H measurement than the electrometric methods so widely used.

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Book reviews

ABSORPTIOMETRIC ANALYSIS

Metallurgical Analysis by Means of the Spekker Photo-electric Absorptiometer, *by F. W. Haywood and A. A. R. Wood. Pp.* 128. *Adam Hilger Limited, London.* 1944. 18*s. net.*

When a beam of light is passed through a coloured solution the fraction of the light absorbed bears a simple relation to the concentration of the coloured substance and to the thickness of the absorbing layer. This is the basis of colorimetric methods of analysis, in which a comparison is made with a standard solution. By using a photo-electric cell the amount of transmitted light may be measured directly, and by interposing filters, each of which transmits only a definite portion of the spectrum, the concentration of several different coloured salts in a single solution may be determined. This is 'absorptiometric' analysis, for which the Spekker instrument is designed. Light from a constant source is passed through a cell containing the coloured solution, and another beam from the same source passes through an exactly similar cell containing water. The two beams fall on photo-electric cells opposed to one another, so that the difference between the two currents is a measure of the concentration of the substance in question. Chemical analysis is then reduced to the reading of a galvanometer, the calibration of the instrument for each element having been done once for all and embodied in a chart or table. For certain analyses it is better to use, instead of white light from a tungsten lamp, the discontinuous spectrum of a mercury lamp, any line of which may be isolated by interposing an appropriate filter. Analyses made in this way are very rapidly performed and are comparable in accuracy with ordinary chemical methods. The element to be estimated must be capable of forming a coloured compound. Manganese, for instance, is converted to the purple permanganate, copper into a blue cuprammonium salt, nickel into its crimson compound with dimethylglyoxime, and so on. Silicon, itself forming colourless compounds, will give a blue solution when converted into a silicomolybdate and reduced by stannous chloride. The saving of time is very great. As an example, a single weighing of drillings from a high-speed tool steel will furnish a solution in which, by using filters (and for some of the elements adding specific reagents), manganese, chromium, vanadium, copper, cobalt, nickel, and molybdenum may be estimated, whilst two more weighings are required for silicon and titanium, which need different solvents. Similar schemes are submitted for non-ferrous alloys having as their base copper, aluminium, or magnesium.

The technique of this valuable method has been mainly devised since 1941 by the staff of the Admiralty Laboratory at Sheffield. The present authors have given a very clear and detailed account of the use of the Spekker instrument, and the tabular schemes make it easy to apply the method to any alloy. An interesting note deals with its possible extension to nephelometry and with the further development of indirect methods applicable to elements which normally form only colourless salts.

C. H. DESCH

USES FOR SMALL COAL

Problems in the Utilization of Small Coals. *Pp.* 294. *Proceedings of a Conference held at the Institution of Civil Engineers, London, on 10th and 11th November, 1943, by the British Coal Utilization Research Association, Rickett Street, London.* 1944. *N.p.*

The Conference was divided into three sessions, and, of the twenty-eight papers presented, eleven were devoted to the utilization of small coals and slurries, ten to fuels of high inert content, and seven to the 'up-grading' of fuels.

There is no doubt that these problems are of great importance to the nation, because it is vital—particularly at the present time—to make the best use of fuels which in pre-war days were apt to be looked upon with disfavour on account of their high ash and moisture content. In one paper, for example, it is pointed out that some 25 million tons of coal below ¼ in. in size are unavoidably produced each year in Great Britain during the ordinary course of mining, and suggestions are made for using this material. It is also of interest to note that the brickmaking industry may be able to provide an outlet for 'fines,' since about 2½ million tons of coal were used in 1938 for firing some seven thousand million bricks.

Among other fuels dealt with in the first session were anthracite duff and coke breeze, of which over 2 million tons are produced annually by gasworks and coke-ovens.

In view of the large amount of 'slurry' available, the papers in Session 2 are of considerable interest, while the various methods, described in the last Session, for reducing inert matter and rendering certain grades of fuel suitable for use, present an up-to-date picture. The text is enriched by numerous figures, tables of data, and flow-diagrams, while the discussions following the Sessions are included together with author and subject indexes.

ARTHUR MARSDEN

A GUIDE TO HYDROCARBON LITERATURE

Encyclopedia of Hydrocarbon Compounds, *by J. E. Faraday. Volume I. Chemindex Limited, Manchester.* 1945. £7 10*s.*

The encyclopedia lists the methods of preparation and certain properties of the hydrocarbons up to C_8, classified on the Richter formula index system and arranged in a loose-leaf binder which it is intended to keep up to date by the issue of annual supplementary sheets for inclusion or substitution in the parent volume.

Faraday's encyclopedia (which will inevitably be compared with Beilstein, and will suffer from the comparison) cannot have a wide appeal among organic chemists on account of its limited scope; and until it is expanded to cover the whole field of organic compounds, it will be condemned as incomplete even more strongly than Beilstein is condemned as out of date. Among detailed points to which attention may be drawn are (*a*) a list of methods of preparation (e.g. 319 in the case of butadiene) is presented from which the reader must take his choice, unaided by a recommendation such as is offered by Beilstein's *Darstellung*; (*b*) certain physical properties are listed, but no reactions; (*c*) references give no authors' names and in the absence of the original journal it will usually be impossible to find an abstract of the relevant paper; and (*d*) the completeness claimed cannot be substantiated: in a test search of the literature under *iso*propenylacetylene, in addition to the seven preparative methods listed (one of which is incorrectly so described), four more methods were found, all of 1942 or earlier.

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